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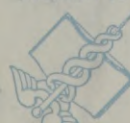
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EXAMINATION OF WATER.

LEFFMANN AND BEAM.

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EXAMINATION OF WATER

FOR

SANITARY AND TECHNICAL PURPOSES,

BY

HENRY LEFFMANN, M.D., PH.D.,

PROFESSOR OF CHEMISTRY IN THE WOMAN'S MEDICAL COLLEGE OF PENNSYLVANIA,
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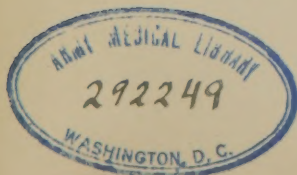
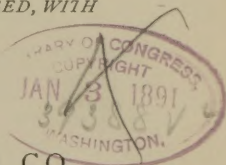
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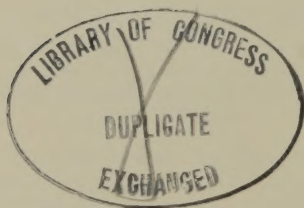
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PREFACE.

IN the period that has elapsed since the publication of the first edition of this work, many processes for water analysis have been proposed, and we have included in the present revision such of these as seem to us of substantial value. In particular we may mention the methods recommended by the Chemical Section of the American Association for the Advancement of Science, and the application of the Kjeldahl process to the determination of the organic nitrogen. The adoption of the former methods will serve to secure uniformity in analytical data, while it is to be hoped that chemists generally will investigate and report on the latter, in order that a basis for the interpretation of results may be obtained.

No material change has been made in the description of the general Quantitative Analysis, in which we have followed to a large extent the methods indicated by Fresenius, selecting those best adapted to technical purposes.

We have extended considerably the section on the Biological Examinations, although we have seen no reason to change the opinions expressed in the former edition as to the value of these results. It would be impossible to overestimate the importance of bacteriology, in etiology, pathology and general biology, but until pathogenic microbes are more clearly indicated and described, the

methods will be of little use in dealing with the problem of the determination of the sanitary and technical value of water supplies.

In the chapter on the Purification of Water we have described in some detail a few of the important systems, especially the Anderson iron process, the efficiency of which we have had ample opportunity to observe by experiments on a comparatively large scale, extending over several months.

The favorable reception accorded to the first edition, both by journals of acknowledged authority, and by chemists of extended experience in this department, has indicated that the work is not without usefulness in the field to which it is devoted.

H. L.

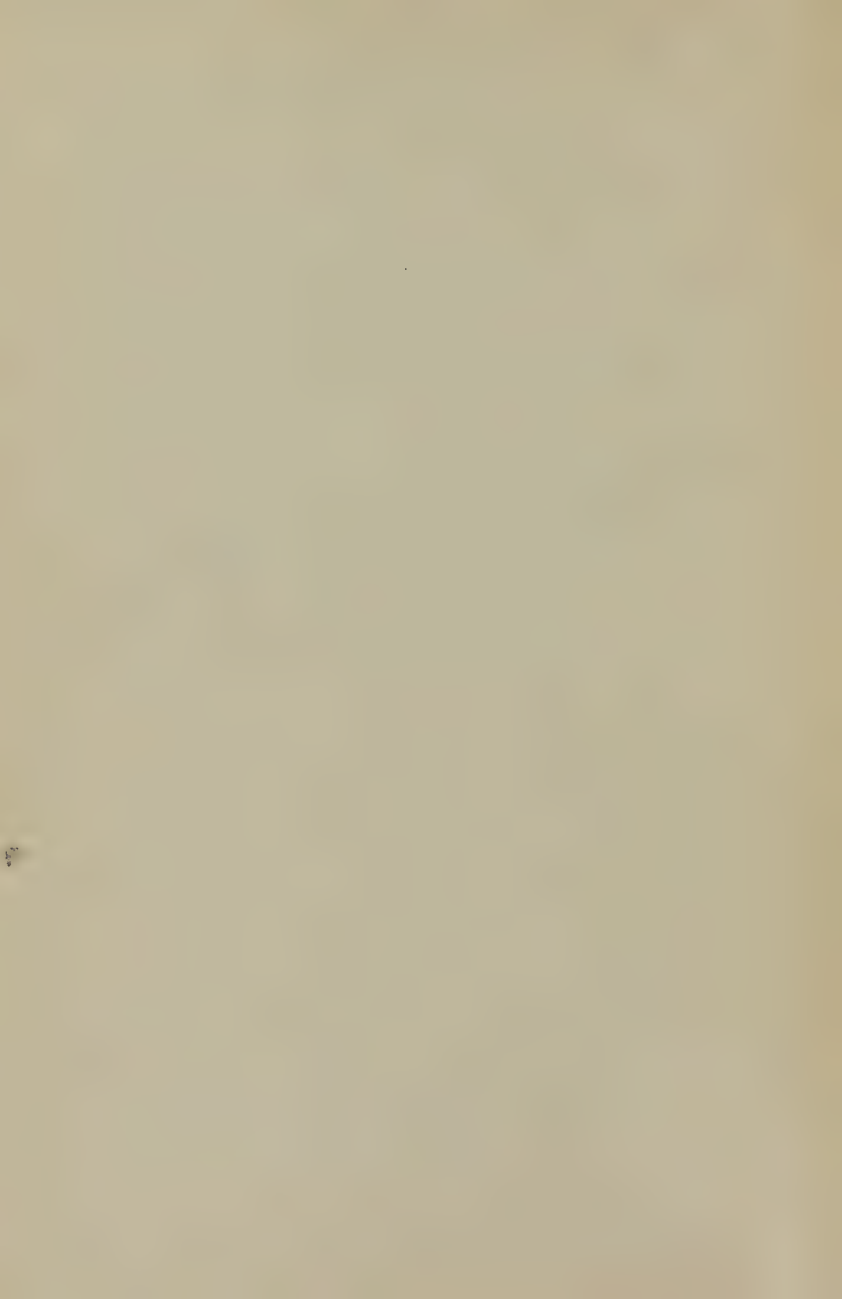
W. B.

715 Walnut St.

December, 1890.

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EXAMINATION OF WATER.

HISTORY OF NATURAL WATERS.

Pure water is an artificial product of the laboratory. Natural waters always contain foreign matters in solution and suspension, varying from mere traces to very large proportions. The properties, effects and uses of water are considerably modified by these ingredients, and the object of analysis is to ascertain their character and amount. Since these are largely dependent on the history of the water, a classification based on this will be convenient. We may distinguish four classes of natural waters:—

Rain Water.—Water precipitated from the atmosphere under any conditions, and therefore including dew, frost, snow and hail.

Surface Water.—All collections of water in free contact with the atmosphere, as in streams, seas, lakes, or ponds.

Subsoil or Ground Water.—Water not in free contact with the atmosphere, percolating or flowing through soil or rock at moderate distance below the surface, and derived in large part from the rain or surface water of the district.

Deep or Artesian Water.—Water accumulated at considerable depth below the surface, from which the subsoil water of the district has been excluded by difficultly permeable strata.

Rain Water, when gathered in the open country and

in the latter period of a long rain or snow, is the purest form of natural water. When collected directly, it contains but little solid matter, this consisting principally of ammonium compounds and particles of organic matter, living and dead, gathered from the atmosphere. In districts near the sea an appreciable amount of chlorides will be present. It is obvious that a prolonged rain will wash out the air, but since storms are usually attended by wind, fresh portions of air are continually flowing in, and thus the water never becomes perfectly pure. Rain water collected in inhabited districts is usually quite impure.

Surface Water.—Rain water in part flows off on the surface, and gains in the proportion of suspended and dissolved matters, the former being found in large amount when the rainfall is profuse. The wearing action of water is dependent on the amount and character of these suspended materials. From the higher levels of a watershed, the streams, more or less in the form of torrents, gather into larger currents, and reaching lower levels become slower in movement, and deposit much of the suspended matter. By admixture of the waters from widely separated districts the character and amount of the dissolved matters are much modified. An action of this kind is seen in the watershed of the Schuylkill River. This stream rises in the anthracite-coal region of Pennsylvania, and receiving much refuse mine-water becomes impregnated with iron salts and free mineral acid, being then quite unsuitable for drinking or manufacturing purposes. In its course of about one hundred miles, it passes over an extensive limestone district, and receives several large streams highly charged with calcium carbonate. The result is a neutralization of the acid, and a precipitation of the iron and much of the calcium. The river

becomes purer, and at its junction with the Delaware River at Philadelphia, it contains neither free sulphuric nor hydrochloric acid, only traces of iron, and but a small amount of calcium sulphate. In this manner there is produced a soft water, superior to that of the river near its source, or to the hard waters of the middle Schuylkill region.

It is obviously impossible to establish close standards of composition for surface waters. In the case of rain water, falling on the surface of undisturbed, unpopulated territory, the amount of solids dissolved will be small, and will consist principally of carbonates and sulphates. The water of lakes and rivers is, however, in part derived from springs, which may proceed from great depths, and thus introduce substances not easily soluble in surface water, nor derivable from the soil of the district.

The exposure to light and air which surface water undergoes, results in the absorption of oxygen and loss of carbonic acid, together with the oxidation of the organic matter. The diminution of the rapidity of the current permits the deposition of the suspended matters, and this occurs especially as the river approaches the sea, not only from the retarding influence of the tidal wave, but from the precipitating action of the salt water. The investigations of Carl Barus, published in Bulletin No. 36, U. S. Geological Survey, have shown the decided influence of sodium chloride in accelerating the subsidence of fine particles.

Subsoil Water.—Water which penetrates the soil, passes to various depths, according to the porosity and arrangement of the strata. As a rule, it descends until it reaches but slightly pervious formations, upon the level of which it accumulates. In the upper layer of soil it dissolves mineral and organic ingredients, and becomes impregnated

with microorganisms, through the agency of which the organic matter undergoes important transformations. The water constantly accumulating, gradually flows along the incline of the impervious stratum, or through its fissures, and may either pass downward or emerge in the form of a spring.

The proportion of water which may be held by any rock or soil is often much larger than would be at first supposed. T. Sterry Hunt states that a square mile of sandstone 100 feet thick will contain water sufficient to sustain a flow of a cubic foot a minute for more than thirteen years.

Much difference is observed in the composition of sub-soil waters, but as a general rule they contain but a limited amount of mineral substances, and a very small proportion of organic matter. In populated districts, however, a marked change is produced through admixture with water containing animal and vegetable products in various stages of decomposition. It is especially the organic matter containing nitrogen that is of importance. To this class belong all those compounds forming tissues that are intimately associated with vital action; also many characteristic excretory products. These bodies are mostly unstable, and as soon as their vitality ceases begin to decompose, partly by oxidation, partly by splitting up into simpler forms; these changes being in most cases brought about by microorganisms. Among the products noticed in the early stages of such decay, are substances which possess close analogies to the organic bases or alkaloids, but more susceptible of decomposition. They are generally present in minute amount, but are not infrequently very active in their physiological effect. From the most recent researches it seems probable that the pathogenic power of many micro-

organisms rests not upon any mechanical or other action of the germs themselves, but upon the alkaloidal principles which they produce and excrete. As a group these bodies are known as the "ptomaines." Nitrogen is an invariable ingredient. The ultimate results of the processes of decomposition depend largely on circumstances. When organic matters containing nitrogen are subjected to the action of oxidizing agents, such as alkaline potassium permanganate or chromic acid, some of the nitrogen is converted into ammonia. A similar result occurs in all waters, but a considerable portion of the organic matter may also suffer further oxidation and in association with the mineral substances present form nitrites and nitrates, especially the latter. This conversion is called "nitrification." The conditions under which it occurs have been carefully studied by Warrington, Munro and others.

Nitrification takes place under the influence of microbes, the habitat of which does not extend more than a few yards below the surface of the soil. Percy and Grace Frankland have isolated and described a bacillus with active nitrifying powers. It is a very short, almost spherical form, which grows in ammoniacal culture-fluids and in meat-broth, but does not grow in the usual gelatin-peptone mixture, except when previously cultivated in meat-broth. The nitrifying action is probably exerted only upon the ammonium which is formed from the organic matter. The presence of some substance capable of neutralizing acids is necessary to continuous action. Calcium and magnesium carbonates fulfill this function. Nitrates are the final result of this action; nitrites are present at any given time only in small quantity. Denitrification, that is, the reduction of nitrates and nitrites to ammonium, takes place under

the influence of microbes, and is especially apt to occur when considerable quantities of decomposing organic matter are introduced. Percy and Grace Frankland have described several species of bacilli which have active denitrifying powers. Among these are *Bacillus liquidus*, *B. vermicularis* and *B. ramosus*. A partial reduction sometimes occurs, and a notable proportion of nitrites is found, but in the presence of actively decomposing organic matter, such as that in sewage, a complete reduction, even to the liberation of nitrogen, may occur.

Deep Water.—Water which penetrates the fissures of the fundamental rock formations may pass to great depths, and by following the lines of the lowest and least permeable strata may be transported to points far removed from those at which it was originally collected. The chemical changes thus induced include most of those which take place at higher points, but the increase of pressure and temperature confers increased power. Carbonic acid will accumulate under conditions favorable to the solution of calcium, magnesium and iron carbonates, and iron and manganese oxides may be converted into carbonates and then dissolved. Sulphates are reduced to sulphides, and these subsequently, by the action of carbonic acid, yield hydrogen sulphide. Organic matter, living and dead, plays an important part, determining the reduction of ferric compounds to ferrous, and of the sulphates to sulphides, and is itself converted ultimately into ammonium compounds, notable quantities of which are often found in deep waters. Further, it is found that nitrates and nitrites are present only in small amount, except from certain strata rich in organic matter. In some cases the water acquires very high temperature, and dissociation of rocks occurs,

with solution of considerable amounts of silicic acid, which is ordinarily but sparingly soluble in water.

Masses of water thus accumulated under heat and pressure may find their way to the surface either through natural fissures, or be reached by borings. The mineral springs, highly charged with solid matters, and the artesian waters, are obtained in this way.

While no absolute unchangeable line can be drawn between deep and subsoil waters, yet it will in most cases be found that the deep water of a given district, whether obtained through natural or artificial channels, will be decidedly different in composition from the subsoil or surface water of the same, and that the rocks passed through in such cases will be characterized by one or more strata, difficultly permeable to water, and therefore preventing direct communication. The characteristic differences between surface, subsoil, and deep waters are clearly indicated in the table of analyses made by us as given in the Appendix.

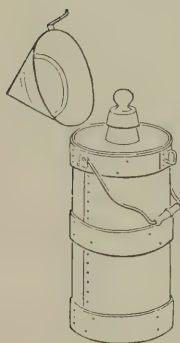
The fact that mere depth is not the essential difference between the two classes of waters is shown by comparison between the composition of the water from the well at Barren Hill, on the northern border of Philadelphia county, and the deep well at Locust Point, Baltimore. The former is a dug well, 130 feet deep; the latter is an artesian boring of 128 feet, which in its descent passes through four feet of solid rock. The deeper well is evidently supplied by subsoil water. The artesian well, though located 100 yards from a brackish sewage-laden estuary, evidently derives no water from it.

ANALYTICAL OPERATIONS.

SANITARY EXAMINATIONS.

COLLECTION AND PRELIMINARY EXAMINATION OF SAMPLES.

FIG. 1.



Great care must be taken in collecting water samples, in order to secure a fair representation of the supply and to avoid introduction of foreign matters. The five-pint green glass stoppered bottles used for holding acids are suitable for containing the samples. The contents of one such bottle will suffice for most sanitary or technical examinations. Fig. 1 shows a bottle encased in wood, and known under the name of the "Penn Demijohn," which we have found very convenient for transportation. It is provided with a hinged lid which can be securely fastened by a padlock. The green glass stoppered bottles may also be fitted to such an arrangement. Stone jugs, casks or metal vessels must not be employed. The bottles used must be thoroughly rinsed several times with the water to be examined, filled and the stopper tied down, or fastened by stretching a rubber finger-cot over the stopper and lip. If corks are used, they should be new and thoroughly rinsed. No wax, putty, plaster or similar material should be used.

In taking samples from lakes, slow streams or reservoirs, it is necessary to submerge the bottle so as to avoid collecting any water that has been in immediate contact with the air.

In the examination of public water supplies, the sample should be drawn from a hydrant in direct connection with the main, and not from a cistern, storage tank or dead end of a pipe. In the case of pump-wells, a few gallons of water should be pumped out before taking the sample, in order to remove that which has been standing in the pipe.

In all cases care should be taken to fill the vessel with as little agitation with air as possible.

It is important that with each sample a record be made of those surroundings and conditions which might influence the character of the water, particularly in reference to sources of pollution, such as proximity to cesspools, sewers or manufacturing establishments. The character and condition of the different strata of the locality should be noted if possible.

Determinations of nitrogen existing as ammonium compounds, and as organic matter, and of oxygen-consuming power, should be made upon the sample in the original condition, whether turbid or clear, but all other estimations should be made upon the clear liquid. Turbid waters may be clarified by standing or by filtration ; for the latter purpose Schleicher & Schüll's extra heavy No. 598 paper is the best. In many cases the suspended matter cannot be entirely removed by filtration, and subsidence must be resorted to. The use of a small quantity of alum, as described in the section on the purification of water, will sometimes be applicable as a rapid means of clarifying water samples. For the quantitative determination, the sediment from a

known volume of the water is collected on a tared filter, dried at 112° F., and weighed.

The water from newly-dug wells is generally turbid and the determinations are best made after filtration, but the results will be unsatisfactory, showing a higher proportion of organic matter than will be found when the supply becomes clear.

The following methods of determining color and odor have been adopted by the Society of Public Analysts of Great Britain:—

Color.—A colorless glass tube, 2 feet long and 2 inches in diameter, is closed at each end with a disc of colorless glass. An opening for filling and emptying the tube should be made at one end, either by cutting a small segment off the glass disc, or cutting out a small segmental section of the tube itself before the disc is cemented on. A good cement for such purposes is the following:—

| | |
|-----------------------|----------|
| Caoutchouc, | 2 parts. |
| Mastic, | 6 “ |
| Chloroform, | 100 “ |

The ingredients are mixed and allowed to stand for a few days. The cement should be used as soon as solution is effected, as it becomes viscid on standing.

The tube must be about half filled with the water to be examined, brought into a horizontal position, level with the eye, and directed toward a brightly illuminated white surface. The comparison of tint has to be made between the lower half of the tube containing the water under examination, and the upper half containing air only.

Odor.—Put about 150 c. c. of the water into a clean, wide-mouth 250 c. c. stoppered bottle, which has been

previously rinsed with the same water ; insert the stopper and warm the water in a water-bath to 100° F. Remove the bottle from the water-bath, and shake it rapidly for a few seconds ; remove the stopper and immediately note if the water has any smell. Insert the stopper and repeat the test.

In a polluted water the odor will sometimes give a clue to the origin of the pollution.

Reaction.—The determination of reaction is usually made by the addition of a neutral solution of litmus to the water. If an acid reaction is obtained the water should be boiled in order to determine if it is due to carbonic acid. Some of the more delicate indicators, such as phenolphthaleïn and lacmoid, may be used with advantage for these tests. The latter possesses the advantage that it is unaffected by carbonic acid, but detects even traces of free mineral acid. It is neutral, also, to many normal metallic salts, such as ferrous sulphate, which are acid to litmus. Ferric salts, however, are acid to lacmoid. Its color changes are the same as those of litmus, *i. e.*, red with acids and blue with alkalies.

Phenolphthaleïn is best applied to the detection of weak acids, such as carbonic acid and the organic acids. In acid and neutral solutions it is colorless—in alkaline, deep red. Nearly all waters contain carbonic acid, and will therefore bleach a solution of phenolphthaleïn which has been reddened by a small amount of alkali.

TOTAL SOLIDS.

A platinum basin holding 100 c. c. will be found convenient for this determination. This should weigh about 45 grams. It should be kept clean and smooth by frequent

burnishing with sand, a little of which should be placed in the palm of the hand, moistened, and the dish gently rubbed against it. Very fine sea sand with round, smooth grains is the only kind suitable for this purpose. Coarse river sand, tripoli, or other rough scouring powders, must not be employed. If proper care is taken, the lustre of the metal will remain unimpaired indefinitely, and the loss in weight will be trifling. The inner surface can generally be cleaned by treatment with hydrochloric acid, rinsing and, if necessary, burnishing. Neglect of these precautions will soon lead to serious damage to the dish. A small, smooth slab of iron or marble is convenient to set it on while cooling. When being heated over the naked flame the dish should rest on a triangle of iron wire, covered with pipe-stems. The dishes of pure nickel have not been found by us to be satisfactory substitutes for those of platinum.

Platinum-pointed forceps should be used in handling the dish. The platinum terminals may be kept bright and clean by the use of sand.

FIG. 2.



The low-temperature burner, used as shown in Fig. 2, will be found a very convenient substitute for the water-bath and hot air oven. The inlet pipe is very short and soon becomes so hot as to injure the rubber tube. To avoid this it may be lengthened by means of a piece of $\frac{1}{8}$ inch gas-pipe, or the junction may be

wrapped with a rag, the ends of which dip into water. By capillary attraction the rag is kept moist and cool.

The determination of total solids is made by evaporating 50 or 100 c. c. of the water in the platinum basin, which has been previously heated almost to redness, allowed to cool for ten minutes, and weighed. The operation is conducted at a moderate heat. When the residue appears dry, the heat may be increased slightly for some minutes. The above method will answer in most cases. In waters of exceptional purity it may be advisable to use larger quantities, such as 250 c. c. When the residue contains deliquescent bodies, the determination will not be accurate, and when bodies are present which take up much water of crystallization, the residue will need to be strongly heated, if control figures are to be obtained. This determination of total solids is described in connection with the technical examinations.

After the weight of the residue is obtained, the dish should be cautiously heated to low redness, and the effect noted. Nitrates and nitrites, calcium and magnesium carbonates, and magnesium chloride are decomposed; ammonium salts are driven off; potassium and sodium chlorides are also driven off if the temperature is high. Organic matter is at first charred, and by continued heating burned off. When the quantity of nitrates is considerable, slight deflagration may be observed, or the production of red fumes of nitrogen dioxide. The organic matter, in decomposing, not infrequently develops odors which indicate its character or source. These are more satisfactorily observed, when a rather large quantity, say 250 c. c., is evaporated at a low heat, preferably on a water-bath.

In water of high organic purity, the residue on heating will give no appreciable blackening nor odor, while in

forest streams charged with vegetable matter derived from falling leaves, very decided blackening without unpleasant odor will be noticed. The loss of weight after heating cannot be taken as a measure of the organic matter, except when present in relatively large amount.

CHLORINE.

Solutions Required :—

Standard Silver Nitrate.—Dissolve about 5 grams of pure recrystallized silver nitrate in distilled water, and make the solution up to 1000 c. c. The amount of chlorine to which this is equivalent may be determined as follows: Several grams of pure sodium chloride are finely powdered and heated over a Bunsen burner for five minutes, not quite to redness. When cold, 0.824 gram is dissolved in water and the solution made up to 500 c. c. 25 c. c. of this should be treated as below, and the amount of silver solution required noted. Each c. c. of the sodium chloride solution is equivalent to .001 gram chlorine.

Potassium Chromate.—5 grams of potassium chromate are dissolved in 100 c. c. of distilled water. A solution of silver nitrate is added until a permanent red precipitate is produced, which is separated by filtration.

Analytical Process :—

If a preliminary test shows the chlorine to be present in considerable amount, the determination may be made on 100 c. c. of the water without concentration. If, however, there is but little present, 250 c. c. should be evaporated to about one-fifth, and the determination made on the concentrated liquid after cooling.

The water is placed in a porcelain dish or in a beaker standing on a white surface, a few drops of potassium

chromate solution added, and standard silver nitrate solution run in from a burette until a faint red color of silver chromate remains permanent on stirring. The proportion of chlorine is then calculated from the number of c. c. of silver solution added. For greater accuracy a second determination may be made, using as a comparison the liquid first titrated, the red color having been previously discharged by a few drops of sodium chloride solution.

The water should always be as nearly neutral as possible before titration. If acid, it must be neutralized by the addition of some precipitated calcium carbonate.

NITROGEN IN AMMONIUM COMPOUNDS AND IN ORGANIC MATTER.

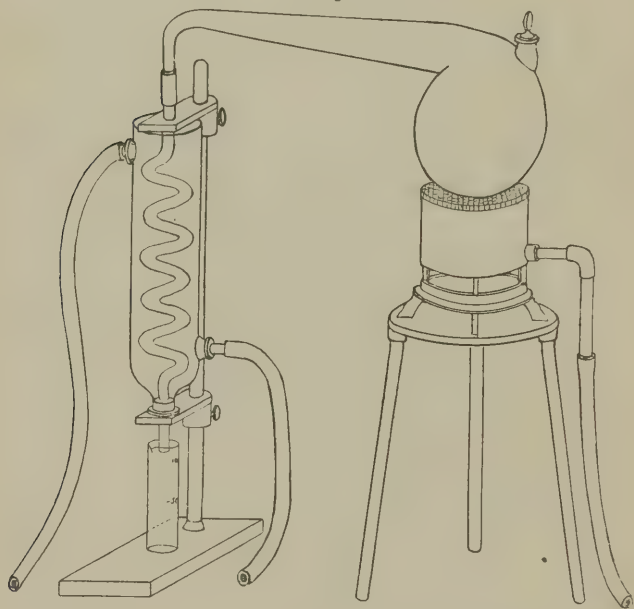
The nitrogen in ammonium compounds, and a part of that in the organic matter, is determined by a process of distillation first developed fully by Messrs. Wanklyn, Chapman and Smith. It depends upon the conversion of the nitrogen into ammonia and subsequent estimation in the distillate.

Apparatus Required :—

Distilling Apparatus.—That shown in Fig. 3 has been found to be the most convenient. The still consists of a Bohemian glass retort of about 1000 c. c. capacity. The beak of the retort should incline slightly upward, to prevent contamination by splashing. At about two inches from the end it should be bent at a right angle, and drawn out so as to enter the condensing worm for about an inch, and terminate beneath the level of the water. Glass worms are apt to crack, and it is more satisfactory to use one of block tin. A piece of rubber tubing is drawn over the junction.

A rapid current of cold water should be maintained through the condenser. The heat is applied by means of the low-temperature burner, the iron ring of which is removed so that the retort rests directly on the gauze. With this

FIG. 3.



arrangement the heat is under perfect control, and the danger of fracturing the glass is reduced to a minimum.

Cylinders for Comparison-Color Tests, about 2.5 cm. in diameter and holding 100 c. c., made of colorless glass.

Solutions Required :—

Sodium Carbonate.—50 grams of pure sodium carbonate

are strongly heated, dissolved in 250 c. c. of distilled water, and the solution boiled down to 200 c. c.

Ammonium-Free Water.—If the distilled water of the laboratory gives a reaction with Nessler's reagent, it should be treated with sodium carbonate, about one grain to the liter, and boiled until about one-fourth has been evaporated. Ammonium-free water may be obtained by distilling in a retort, water made slightly acid with sulphuric acid.

Standard Ammonium Chloride.—Dissolve 0.382 gram of pure dry ammonium chloride in 100 c. c. of ammonium-free water. For use, dilute 1 c. c. of this solution with pure water to 100 c. c. 1 c. c. of this dilute solution contains .00001 gram of nitrogen.

Nessler's Reagent.—Dissolve 35 grams of potassium iodide in 100 c. c. of water. Dissolve 17 parts of mercuric chloride in 300 c. c. of water. The liquids may be heated to aid solution, but must be cooled before use. Add the mercuric chloride solution to that of the potassium iodide, until a permanent precipitate is produced. Then dilute with a 20 per cent. solution of sodium hydroxide to 1000 c. c., add mercuric chloride solution until a permanent precipitate again forms and allow to stand until clear. Nessler's and other reagents are best kept in glass-capped bottles, Fig. 4, in which the pipette may remain when not in use. The solution improves by keeping.

FIG. 4.



Alkaline Potassium Permanganate.—Dissolve 200 grams of potassium hydroxide, in sticks, and 8 grams of potassium permanganate, in a liter of distilled water.

The solution is boiled until about one-fourth is evaporated; then made up to a liter with ammonium-free

water. Since it will still furnish some ammonia, it is necessary to determine the amount. Fox recommends to distill 50 c. c. with 500 c. c. of absolutely ammonium-free water, best twice distilled with sulphuric acid, and note the ammonia obtained. This quantity should be deducted in each analysis.

Analytical Process :—

The retort and condenser are thoroughly rinsed with ammonium-free water, 500 c. c. of the water to be tested introduced, about 5 c. c. of the sodium carbonate solution added to render the water alkaline, and a piece of pumice-stone heated to redness and dropped in while hot. The water is then boiled gently until the distillate measures 50 c. c. The distillate is transferred to one of the color-comparison cylinders and 2 c. c. of the Nessler's reagent added. A yellowish-brown color is produced, the intensity of which is proportional to the amount of NH_3 , present. The full color is developed in five minutes. This color is exactly matched by introducing into another cylinder 50 c. c. of ammonium-free water, some of the standard ammonium chloride solution, and 2 c. c. Nessler's reagent, as before. According as the color so produced is deeper or lighter than that obtained from the water, other comparison liquids are prepared containing smaller or larger proportions of the ammonium chloride, until the proper color is produced.

The distillation is continued, successive portions of 50 c. c. each collected, and tested until no reaction occurs with Nessler's reagent. The sum of the figures from the several distillates gives the total nitrogen obtainable as "free ammonia," so-called.

If the quantity of ammonia is sufficient to cause a precipi-

tate, the color comparison cannot be accurately made. In most cases this will not be of serious moment, as the quantity will be beyond the allowable limit. If accurate determination be desired, it may be made by dividing the first distillate into two equal parts, nesslerizing one of these, and then, if necessary, diluting the second part with ammonium-free water and nesslerizing this.

Occasionally the evolution of ammonia continues indefinitely, and may even increase with successive distillates. This is due, not to ammonium compounds existing as such, but to decomposition of certain nitrogenous bodies, especially urea. In this case, it is not advisable to prolong distillation beyond the fourth or fifth distillate, but to proceed to the following part of the process.

The residue in the retort serves for the determination of the nitrogen which is convertible into ammonia by alkaline potassium permanganate—the so-called “albuminoid ammonia” of Messrs. Wanklyn, Chapman and Smith.

50 c. c. of alkaline permanganate solution are added to the retort, the distillation resumed, and the nitrogen estimated in each 50 c. c. as before, deducting that yielded by the permanganate.

It is the practice of some analysts to mix the distillates of each of the above operations, and thus make determinations merely of the total nitrogen in each case. By so doing valuable information may be lost, since it has been pointed out by several observers, notably Mallet and Smart, that important information may be gained by observing the rate of evolution of the ammonia. Mallet has further pointed out that many waters may contain substitution ammoniums which may pass over before the addition of the alkaline permanganate, but not be correctly measured by

nesslerizing. To avoid this source of error, he suggested that two determinations be made on each sample, one as above described and the other by the addition of alkaline permanganate without previous distillation. In this manner a higher figure will often be obtained than the sum of the figures from the two distillations by the other process.

Since small quantities of ammonium compounds and nitrogenous matters are everywhere present, the greatest care should be exercised in order to avoid their introduction in any way during the course of the analysis. All measuring vessels, cylinders, etc., should be thoroughly rinsed before using.

The Chemical Section of the American Association for the Advancement of Science recommends the following method for the application of the "ammonia process," embodying the results of recent investigations:—

"200 c. c. of distilled water, together with 10 c. c. of the sodium carbonate solution, are distilled down to about 100 c. c. in the retort in which the analysis is to be conducted, and the last portion of 50 c. c. nesslerized to assure freedom from ammonia. Then 500 c. c. of the water to be examined are added and the distillation is carried on at such a rate that about 50 c. c. are collected in each succeeding ten minutes, and until a 50 c. c. measure of distillate is obtained containing only an inappreciable quantity of ammonia. In nesslerizing, five minutes are to be allowed for the full development of color; after this, no change takes place for many hours.

"Now throw out the contents of the retort, rinse it thoroughly, put in 200 c. c. of distilled water and 50 c. c. of the permanganate solution, distill down to about 100 c. c., and nesslerize the last portion of 50 c. c., to make sure of

freedom from ammonia; add another portion of 500 c. c. of the water under examination and proceed with the distillation and nesslerizing as with the first portion.

“The difference between the ‘free’ ammonia of the first operation and the total ammonia of the second, is to be taken as the ‘albuminoid’ ammonia.”

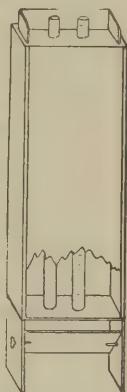
For nesslerizing and other color comparisons, many forms of apparatus have been proposed. One of the simplest is that devised by Hehner, shown in Fig. 5. It consists of a graduated cylinder with a stopcock near the base, by which the liquid can be drawn down at will. Two such cylinders may be used, one for the nesslerized distillate, the other for the comparison liquid. The darker liquid is drawn out until the tints are equal, when the relative volumes remaining will give the data for calculation.

FIG. 5.



Another convenient form of color comparator is shown in Fig. 6. It consists of a box blackened inside, and supported so as to permit a movable mirror to be mounted underneath. The box is perforated at both ends to receive graduated tubes holding 60 c. c. A projecting rim shades the ends of the tubes from extraneous light.

FIG. 6.



In practice the Nessler reagent is mixed with 50 c. c. of the distillate, and poured into one of the tubes. The usual comparison color is made up and transferred to the other tube. The darker liquid is poured into the vessel in which it was originally prepared and then poured slowly back into the tube until the colors are equalized.

This apparatus permits the use of amber glass as a standard color in place of the comparison liquid. Very rapid and sufficiently accurate determinations can be made by this means. The amber glass is standardized as follows:—

One of the tubes is nearly filled with clear water, and the glass placed across the top, the mirror being so adjusted that the light is thrown directly up the tube. The equivalent of the color so produced is carefully determined by nesslerizing, in the adjoining tube, a known amount of ammonium chloride. The glass is used as a comparison color by placing it, as before, on the top of one of the tubes filled with clear water, and pouring into the other tube the distillate mixed with Nessler's reagent until the colors are equalized.

For example: If the glass is equal to 1.5 c. c. standard diluted ammonium chloride solution, and in a given experiment, the tube must be filled to 40 c. c. with the liquid to be determined (50 c. c. of distillate and 2 c. c. of Nessler) then

$40 : 52 :: 1.5 : 1.95$. 1.95 is the number of c. c. of ammonium chloride solution to which the 50 c. c. of distillate are equal.

TOTAL ORGANIC NITROGEN.

Several processes for the determination of the organic nitrogen in water, based on those in use in ordinary organic analysis, have been devised. That of Frankland and Armstrong requires complex and extensive apparatus and special skill, has been shown also to be liable to inaccuracies, and has not come into extended use.

The ease and certainty with which the nitrogen of most organic bodies may be converted into ammonium sulphate

by boiling with sulphuric acid, offers a means of determination free from the objections of former methods. The method introduced by Kjeldahl for general organic analysis, was first successfully applied to water analysis by Drown and Martin (*Technology Quarterly*, 11, 3).

In their original process 500 c. c. was concentrated to about 300 c. c., and the distillate nesslerized for determining the nitrogen existing as ammonium compounds. The organic nitrogen is then determined in the residual water. Owing to the fact that in many waters the organic matter is decomposed by boiling, there is liability to underestimation of the nitrogen. We prefer, therefore, to determine at once the total unoxidized nitrogen, and estimate, without distillation, on a separate portion of the sample, the nitrogen that exists in ammonium compounds. Our procedure is as follows:—

Reagents Required:—

Concentrated Sulphuric Acid.—This should be as free as possible from nitrogen. It can be obtained containing only 0.015 mgm. in 10 c. c.

Sodium Hydroxide Solution.—The white granulated caustic soda sold for household use will answer; 350 grams are dissolved in water and made up to 1000 c. c.

Sodium Carbonate and Hydroxide Solution.—25 grams of each are dissolved in 250 c. c. of distilled water, and the solution boiled down to 200 c. c., to free it from ammonium.

Analytical Process:—

Determination of Nitrogen Existing as Ammonium.—200 c. c. of the water are placed in a stoppered bottle, 2 c. c. each of the solutions of sodium carbonate and sodium hydroxide added, the stopper inserted, the solutions mixed and allowed to stand for an hour or two. A filter is pre-

pared by inserting a rather large plug of absorbent cotton in a funnel. This should be washed with ammonium-free water until the filtrate gives no color with Nessler's reagent. The clear portion of the sample is drawn off with a pipette and run through the filter, the first portions being rejected, since it is diluted by the water retained in the cotton. The filtration is rapid, and when 100 c. c. of the liquid have passed through it is nesslerized. If but little ammonium is present, a narrow tube about 60 centimeters long should be used for observing the color.

Estimation of the Total Organic and Ammoniacal Nitrogen.—500 c. c. of the water are placed in a round-bottomed Bohemian glass flask, 10 c. c. of concentrated sulphuric acid added, and a piece of pumice-stone is heated to bright redness and dropped in while hot. The liquid is boiled until the acid is colorless or very pale, the boiling being continued for nearly an hour from this point. The flask is then removed from the flame, allowed to cool, and about 250 c. c. of ammonium-free water added. 50 c. c. of the sodium hydroxide solution should be placed in the distilling apparatus, Fig. 3, about 250 c.c. of water added, a piece of red-hot pumice-stone dropped in and the liquid distilled until the distillate is free from ammonium. It is best to distill until the retort contains not more than 100 c. c. The sulphuric acid solution is then poured in slowly, by means of a funnel the stem of which touches the side of the retort, so that the two liquids do not mingle. The stopper of the retort is inserted, the liquids mixed by gentle agitation, and distilled. If much ammonium is present it is advisable to distill the first portion into about 10 c. c. of very dilute (1 : 1000) sulphuric acid, a piece of glass tube being connected to the condensing worm so that the lower

end dips below the surface of the liquid. The distillates are collected and nesslerized in the usual way.

A blank experiment should be made to determine the amount of ammonium in the sulphuric acid.

NITROGEN AS NITRATES.

Solutions Required:—

Phenolsulphonic Acid.—37 c. c. of strong sulphuric acid are added to 3 c. c. of water and 6 grams of pure phenol.

Standard Potassium Nitrate.—0.722 gram of potassium nitrate, previously heated to a temperature just sufficient to fuse it, are dissolved in water, and the solution made up to 1000 c. c. 1 c. c. of this solution will contain .0001 gm. of nitrogen.

Analytical Process:—

A measured volume of the water is evaporated just to dryness in a platinum or porcelain basin. 1 c. c. of the phenolsulphonic acid is added and thoroughly mixed with the residue by means of a glass rod. 1 c. c. of water is added, three drops of strong sulphuric acid, and the dish gently warmed on the water bath. The liquid is then diluted with about 25 c. c. of water, ammonium hydroxide added in excess, and the solution made up to 100 c. c.

The nitrate converts the phenolsulphonic acid into picric acid, which by the action of the ammonium hydroxide forms ammonium picrate; this imparts to the solution a yellow color, the intensity of which is proportional to the amount present.

One c. c. of the standard solution of potassium nitrate is now similarly evaporated in a platinum basin, treated as above, and made up to 100 c. c. The color produced is compared to that given by the water, and one or the other

of the solutions is diluted until the tints of the two agree. The comparative volumes of the liquids furnish the necessary data for determining the amount of nitrate, as the following example will show:—

The solution from 10 c. c. is diluted to 100 c. c.; 1 c. c. of the standard, equal to .0001 of N, requires, after treatment, dilution to 200 c. c. to match the color. Then $200 : 100 :: .0001 : x$. $x = .00005 = N$. in 10 c. c. = .005 N. in 1000 c. c.

Since ammonium picrate solution keeps well in the dark, a good plan is to make a solution, equivalent to, say, ten milligrams of nitrogen as nitrate per liter, to which the color obtained from the water may be directly compared.

The results obtained by this method are accurate. Care should be taken that the same quantities of phenolsulphonic acid are used for the water and for the comparison liquid.

With subsoil and other waters probably containing much nitrates, 10 c. c. will be sufficient; but with river and spring waters, 25 c. c. may be used. When the organic matter is sufficient to color the residue, it will be well to purify the water by addition of alum and subsequent filtration, before evaporating.

The following is the process for determining nitrogen as nitrates (and nitrites) recommended by the Chemical Section of the A. A. A. S. It depends upon conversion into ammonium by the copper-zinc couple, and subsequent nesslerizing.

Take two wide-mouth glass-stoppered bottles, each holding 250 c. c. and a piece of sheet zinc as long and about as wide as the bottles are deep from the shoulder down; clean the zinc by dipping in dilute acid and washing with water and make it into a loose coil by rolling it round a piece of

glass tube. Immerse it in a 1.4 to 1.8 per cent. solution of cupric sulphate in ammonia-free water, and leave it there until its surface is well covered with a continuous layer of the black copper; lift it out carefully, cover it in a beaker with successive portions of ammonia-free water, lifting it out and draining each time, and at once put it into one of the bottles of acidified water, prepared as follows:—

Make 500 c. c. of the water to be examined distinctly acid with oxalic acid added in fine powder, with constant stirring, so that it shall dissolve readily, and pour half of the liquid into one of these 250 c. c. bottles, and half into the other, and leave them, stoppered, in a warm place for twenty-four hours. Then nesslerize both samples, decanting off the portions as wanted, from the precipitated earthy oxalates, and using double the usual quantity of Nessler's solution, since the free oxalic acid has to be neutralized first by the alkali of the reagent. The proportion of ammonia may often be so large in the water in which the reduction is made, by the copper-zinc couple, that only five or ten c. c. can be taken for each test, and made up to 50 c. c. by the addition of ammonia-free water. The difference between the results with the two portions of water, gives the amount of nitrogen due to the oxidized nitrogen compounds in the water examined.

NITROGEN AS NITRITES.

The following is Ilosvay's modification of Griess's test. It has the advantage over the original method, that the color is developed more rapidly, and the solutions are not so liable to change.

Solutions Required :—

Para-amidobenzenesulphonic Acid (Sulphanilic Acid).—Dissolve 0.5 gram in 150 c. c. of diluted acetic acid, sp. gr. 1.04.

α -amido-naphthalene Acetate.—Boil 0.1 gram of solid α -amido-naphthalene (naphthylamine) in 20 c. c. of water, filter the solution through a plug of washed absorbent cotton, and mix the filtrate with 180 c. c. of diluted acetic acid. All water used must be free from nitrites, and all vessels must be rinsed out with such water before tests are applied, since appreciable quantities of nitrites may be taken up from the air.

Standard Sodium Nitrite.—0.275 gram pure silver nitrite are dissolved in pure water, and a dilute solution of pure sodium chloride added until the precipitate ceases to form. It is then diluted with pure water to 250 c. c., and allowed to stand until clear. For use 10 c. c. of this solution are diluted to 100 c. c. It is to be kept in the dark.

One c. c. of the dilute solution is equivalent to .00001 gram nitrogen.

The silver nitrite is prepared thus: A hot concentrated solution of silver nitrate is added to a concentrated solution of the purest sodium or potassium nitrite available, filtered while hot and allowed to cool. The silver nitrite will separate in fine needle-like crystals, which are freed from the mother liquor by filtration by the aid of a filter pump. The crystals are dissolved in the smallest possible quantity of hot water, allowed to cool and again separated by means of the pump. They are then thoroughly dried in the water-bath, and preserved in a tightly-stoppered bottle away from the light. The purity may be tested by

heating a weighed quantity to redness in a tared porcelain crucible and noting the weight of the metallic silver. 154 parts of AgNO_2 leave a residue of 108 parts Ag.

Analytical Process :—

25 c. c. of the water are placed in one of the color-comparison cylinders. By means of a pipette, 2 c. c. each of the solutions of sulphanilic acid and amido-naphthalene acetate are dropped into the water. It is convenient to have a pipette for each solution, and to use it for no other purpose.

One c. c. of the standard nitrite solution is placed in another clean cylinder, made up with nitrite-free water to 25 c. c. and treated with the reagents as above.

In the presence of nitrites a pink color is produced. At the end of five minutes the two solutions are compared, the colors equalized by diluting the darker, and the calculation made as explained under the estimation of nitrates.

The reactions consist in the conversion of the sulphanilic acid into diazo-benzene sulphonic anhydride, by the nitrite present ; this compound is then in turn converted by the amido-naphthalene into azo- α -amido-naphthalene-parazobenzene sulphonic acid. The last-named body gives the color to the liquid.

OXYGEN-CONSUMING POWER.

All organic materials being more or less easily oxidized, several methods have been suggested for determining the oxygen-consuming powers of waters by treatment with active oxidizing agents. These methods are, however, limited in value. The organic matters in water differ much in character and condition, and their oxidability is subject to much variation, according to the circumstances

under which the test is made. Nevertheless, as a high oxygen-consuming power certainly indicates departure from purity, some additional evidence may be obtained. Potassium permanganate is especially suitable. The test is usually made by introducing a known amount of the permanganate into the water, which has been rendered acid, and measuring after a definite period the proportion which has been decomposed.

It must not be overlooked that if a water contains nitrites, ferrous compounds, or sulphur compounds other than sulphates, the proportion of oxygen consumed will be greater than that required for the organic matter. It has been proposed, in order to remove the nitrites before applying the permanganate, to take 500 c. c. of the water, add 10 c. c. of the dilute sulphuric acid, boil for twenty minutes, allow to cool, and then treat with permanganate. Since, however, the amount of nitrites, if appreciable, can be directly determined, it is more satisfactory to deduct from the oxygen consumed the amount required to convert the nitrites present into nitrates, and the remainder will be that required for the other oxidizable ingredients. 14 parts of nitrogen existing as nitrite require 16 parts of oxygen for conversion into nitrate. Similarly, 112 parts of iron in a ferrous compound will require 16 parts of oxygen for conversion to the ferric condition.

Of the following methods the first is due in the main to Dr. Tidy, has been improved by Dr. Dupré, and is approved by the Society of Public Analysts of Great Britain :—
Solutions Required :—

Standard Permanganate.—395 gram pure potassium permanganate are dissolved in distilled water, and the solution made up to 1000 c. c. 1 c. c. is equal to .0001 gram oxygen.

Diluted Sulphuric Acid.—Add 50 c. c. of pure sulphuric acid to 100 c. c. of water, and then add solution of potassium permanganate until a faint pink color is obtained, which is permanent when the liquid is heated to 80° Fahrenheit for four hours.

Potassium Iodide.—10 grams of the pure salt recrystallized from alcohol are dissolved in 100 c. c. of distilled water.

Sodium Thiosulphate.—1 gram of the pure crystallized salt dissolved in 2000 c. c. of distilled water.

Starch Indicator.—1 gram of clean starch is mixed smoothly with cold water into a thin paste, then poured gradually into about 200 c. c. of boiling water, the boiling continued for one minute, the liquid allowed to settle, and the clear portion used. It is best freshly prepared.

Analytical Process:—

Two determinations are made, one, of the oxygen consumed in fifteen minutes, which is considered to represent the nitrites, sulphides or ferrous compounds, and the other of the oxygen consumed by four hours' action. Both determinations are made at a temperature of 80° F. Three glass-stoppered bottles, of about 350 c. c. capacity, are rinsed with strong sulphuric acid, and then with water. In one is placed 250 c. c. of pure distilled water as a control experiment, and in each of the others 250 c. c. of the water to be tested. The bottles are stoppered, and brought to a temperature of 80 F. ; 10 c. c. of the dilute sulphuric acid and 10 c. c. of the standard permanganate are added to each and the stoppers again replaced. At the end of fifteen minutes one sample of water is removed from the bath, and two or three drops of the potassium iodide solution added to remove the pink color. After thorough

admixture, the thiosulphate solution is run in from a burette until the yellow color is nearly destroyed, a few drops of the starch solution added, and the addition of the thiosulphate continued until the blue color is quite discharged. If the addition of the thiosulphate solution has been properly conducted, one drop of the permanganate solution will restore the blue color.

The other bottles are maintained at 80° F. for four hours. Should the pink color disappear rapidly in the bottle containing the water under examination, 10 c. c. of the permanganate solution must be added to each bottle, in order to maintain a distinct pink color. At the end of four hours each bottle is removed from the bath, two or three drops of potassium iodide added, and the titration with thiosulphate solution conducted as just described. The calculation is most conveniently made as follows:—

a = number of c. c. required for the control experiment.

b = number of c. c. required for the water under examination.

c = available O in permanganate (.001 for 10 c. c.)

x = oxygen consumed by water.

Then, $a : a-b :: c : x$.

The following method is recommended by the Chemical Section of the American Association for the Advancement of Science:—

“Prepare a solution of potassium permanganate containing 0.1 mgm. of available oxygen to one c. c. and a solution of oxalic acid of such strength as to decompose the permanganate solution, volume for volume, the strength being re-determined from time to time. The water used for making these solutions should be purified, by distillation from alkaline permanganate.

“To 200 c. c. of water to be examined, in a 400 c. c. flask, add 10 c. c. of dilute sulphuric acid (1 : 3) and such measured quantity of the permanganate as will give a persistent color; boil ten minutes, add, if necessary, more permanganate in measured quantities so as to maintain the red color; remove the flask from the lamp, add 10 c. c. of oxalic acid solution to destroy the color, or more if required by the excess of permanganate, and then add permanganate, drop by drop, till a faint pink tint appears. From the total quantity of permanganate used deduct the equivalent of the oxalic acid used, and from the remainder calculate the milligrams of oxygen consumed by the oxidizable organic matter in the water.”

The oxygen-consuming power may also be indirectly estimated by the action of the organic matter upon silver compounds. H. Fleck's method (*Fresenius' Quantitative Analysis, English edition, vol. II, p. 127*) depends upon the reduction produced by boiling the water with alkaline solution of silver thiosulphate and estimation of the unreduced silver. A. R. Leeds (*Lond., Edin. and Dub. Phil. Mag., July, 1883*) gives a method by treating the water with decinormal silver nitrate, exposing to light until it settles perfectly clear, and estimating the reduced silver in the deposit.

These methods are open to practically the same objections as in the use of permanganate, and do not seem to possess any decided advantage. Qualitative results of some interest may occasionally be obtained by the following method: 2 c. c. of a one per cent. solution of silver nitrate, rendered decidedly alkaline by ammonium hydroxide, are added to 100 c. c. of the water in a stoppered bottle, which is then placed in full sunlight for two hours. Waters con-

taining but little organic matter will not show at the end of this period any appreciable tint. The following results will show the character of the test:—

| | |
|---|-------------------|
| Schuylkill water, | no color. |
| “ “ with 0.02 c. c. urine, . . . | red-brown. |
| “ “ with 0.01 c. c. urine, . . . | deep brown. |
| “ “ with 0.25 gram raw sugar, . | no color. |
| Well water, not perfectly pure, but | |
| not unfit to drink, | faint black. |
| “ “ markedly contaminated, . . . | black ppt. almost |
| | immediately. |
| Water from a small stream, quite pure . . . | no color. |

PHOSPHATES.

Solutions Required:—

Ammonium Molybdate.—Ten grams of molybdic anhydride are dissolved in 41.7 c. c. of ammonium hydroxide, sp. gr. 0.96, and the solution is poured slowly, and with constant stirring, into 125 c. c. of nitric acid, sp. gr. 1.20, and allowed to stand in a warm place for several days, until clear.

Analytical Process:—

500 c. c. of the water are slightly acidified with nitric acid, and evaporated to about 50 c. c. A few drops of dilute solution of ferric chloride are added and then ammonium hydroxide in slight excess. The precipitate, which contains all the phosphate, is filtered off and dissolved on the filter by the smallest possible quantity of hot dilute nitric acid. The filtrate and washings should not exceed 5 c. c.; if more, they must be evaporated to this bulk. The liquid is heated nearly to boiling, 2 c. c. of ammonium molybdate solution added, and the liquid kept moderately

warm for half an hour. If the quantity of precipitate is appreciable, it is collected on a small weighed filter, washed with distilled water, dried at 100° F. and weighed. The weight of the precipitate multiplied by 0.05 gives the amount of PO_4 . If the quantity is not sufficient to collect in this manner, it is usually reported, according to circumstances, as "traces," "heavy traces," or "very heavy traces."

SUGAR-TEST.

This method was proposed by Heisch for the detection of a fungus supposed to be peculiar to sewage. It consists in adding to the water a small quantity of sugar, in which the fungus grows with great rapidity. The test is applied as follows:—

A stoppered bottle of about 100 c. c. capacity is rinsed thoroughly with the water to be tested, filled with the clear water, about half a gram of pure crystallized sugar added and the stopper inserted. The bottle is placed in a strong light, and kept at a temperature of about 80° F. At the end of several hours it is examined for the fungus, which, in a good side light, with the bottle against a dark background, is generally easily visible as a distinct turbidity. If examined under a power of 250 diameters, it is found to consist of small spherical cells, having in most cases a bright nucleus. After the lapse of some days these gradually group themselves together something like grapes; they next spread out into strings, with a surrounding wall connecting the cells together; the original cells then seem to break and leave apparently tubular threads joined by branches. In the more marked cases the development of the fungus is accompanied by a distinct odor of butyric acid. Hydrogen sulphide and other gases are also some-

times formed. These odors do not generally appear until after twenty-four hours or longer. Heisch concluded that the cells thus developed were distinct evidence of sewage contamination, but such microörganisms are found in all waters that have been exposed even momentarily to air, and Frankland has shown that their development under these conditions is due to the presence of phosphates. He found that the addition even of minute traces of a phosphate, either as sodium phosphate, white of egg, or animal charcoal, at once determined the growth in saccharine liquids which, before, exhibited no tendency to develop them.

DISSOLVED OXYGEN.

The method here given, a modification of Mohr's, was proposed by Blarez. Our experiments indicate that it is rapid and satisfactory.

Solutions Required:—

Sodium Hydroxide.—40 grams of pure sodium hydroxide to the liter.

Ferrous-Ammonium Sulphate.—40 grams dissolved in about a liter of water, and acidified with a few drops of concentrated sulphuric acid.

Decinormal Potassium Permanganate.—3.156 grams dissolved in a liter of distilled water. The accuracy of this solution should be determined by titration with a known weight of ferrous-ammonium sulphate. One c. c. should be equivalent to .0392 gm. ferrous-ammonium sulphate (.0008 gram of oxygen).

The apparatus employed (shown in Fig. 7) is a globular separator, of about 250 c. c. capacity. Above the bulb is a caoutchouc stopper carrying a cylindrical funnel, of about 12 c. c. capacity, terminating in a tube, $\frac{1}{3}$ inch

calibre, sharply contracted at the outlet to a capillary opening. The tube should project about $\frac{1}{4}$ inch below the stopper. The exact capacity of the apparatus is measured as follows: The bulb is completely filled with water and the stopper inserted; the level of the water will rise slightly in the funnel tube, and should be brought down to its outlet by drawing a little off at the stopcock, after which the water is run into a graduated measure and its volume noted.

Analytical Process :—

35 c.c. of mercury and 10 c.c. of sodium hydroxide solution are put into the bulb, and then sufficient of the water to be tested to fill it. The funnel stopper is inserted and the water which rises into the funnel brought into the bulb by cautiously running out at the stopcock, mercury, the volume of which should be noted. The exact volume of water used is thus known. Five c.c. of the ferrous-ammonium sulphate solution are poured into the funnel, brought into the bulb by running out mercury, and the liquid thoroughly mixed by giving the apparatus a gyratory movement. After standing five or six minutes the oxygen will be completely absorbed; 10 c.c. of the diluted sulphuric acid are now added by the same method. On agitating the bulb the contents become clear. The watery liquid is then transferred to a beaker and titrated with decinormal permanganate. A volume of water equal to that used in the test is poured into another beaker, 10 c.c. each of the sodium hydroxide and diluted sulphuric acid added, and then 5 c.c. of ferrous-ammonium sulphate solution.

FIG. 7.



The resulting liquid is titrated with permanganate. The weight of oxygen corresponding to the difference between the two titrations gives the weight of dissolved oxygen in the liquid employed. From this should be subtracted as correction the amount of oxygen dissolved by a volume of water equal to that of the sodium hydroxide solution used. This is found by reference to the table in the appendix. The amount of dissolved oxygen in the sulphuric acid has no appreciable effect.

Nitrates do not appear to impair the accuracy of this method, and the interfering action of nitrites and other reducing compounds is avoided by the control experiment as detailed.

It is perhaps hardly necessary to add that the exact temperature of the water is to be noted at the time of collection of the sample.

In transferring to the bulb, the water should be agitated as little as possible in contact with the air, in order to avoid the absorption of oxygen. A siphon should be used for this purpose, the lower end being allowed to reach to the bottom of the bulb.

The following modification is suggested as being especially suitable for poorly oxygenated waters: An accurately stoppered bottle, the exact capacity of which is known (about 500 c. c. is a convenient size), is completely filled at the source with the water to be examined, and the stopper inserted so as to drive out all air. The stopper is removed in the laboratory, 50 c. c. of the water drawn off with a pipette, and the water covered immediately with a layer of gasoline previously purified by shaking up several times with a solution of potassium permanganate and diluted sulphuric acid, and washed several times with water.

The sodium hydroxide, ferrous-ammonium sulphate and sulphuric acid are introduced into the water by means of burettes to which long glass delivery tubes are attached. The titration with potassium permanganate is conducted in the same way. The liquid is mixed from time to time, as the solutions are added, by means of a glass rod. In this way the air may be completely excluded throughout the entire operation. The amount of water titrated is, of course, equal to the whole capacity of the bottle, less the 50 c. c. removed by the pipette.

The control experiment on an equal volume of the water, and the correction for the oxygen added with the sodium hydroxide solution, are made as detailed above.

Dupré has employed the determination of free oxygen for the estimation of the proportion of oxygen-consuming microbes. The principle of the method is that pure water, if kept in a closed bottle, will neither gain nor lose oxygen in any length of time, but if organisms capable of causing absorption of oxygen are present, the quantity will decrease.

The experiment is carried out by placing a sample of the water in a clean bottle, and vigorously shaking it to saturate with air. A clean 250 c. c. bottle is completely filled with the water, tightly stoppered, and maintained at a temperature of 68° F. for ten days; the free oxygen remaining is then determined.

POISONOUS METALS.

In this class are included *barium*, *chromium*, *zinc*, *arsenic*, *copper* and *lead*; *manganese* and *iron* also, though not usually classed in this group, are objectionable when present in notable amounts.

Barium is rarely present, and only in water containing no sulphates. It can be detected and estimated by slightly acidifying the water with hydrochloric acid, filtering if necessary, and adding solution of calcium sulphate. The precipitated barium sulphate is collected and weighed in the usual way.

Chromium is rarely present, but may be looked for in the waste waters of dye works and similar sources. To detect it, a considerable volume of the water is evaporated to dryness with addition of a small amount of potassium chlorate and nitrate, transferred to a porcelain crucible and brought to quiet fusion; any chromium present will be found in the residue in the form of chromate. The fused mass, after cooling, is boiled with a little water, filtered, the filtrate rendered slightly acid with hydrochloric acid, and a solution of hydrogen dioxide added. In the presence of chromium a transient blue color will appear; by adding a little ether, and shaking the mixture the color will pass into the ether, and on standing will form a blue layer on the surface of the water.

Zinc is best detected by the test described by Allen. The water is rendered slightly ammoniacal, heated to boiling, filtered, and the clear liquid treated with a few drops of potassium ferrocyanide; in the presence even of the merest trace of zinc a white precipitate will be produced.

Arsenic is most readily detected by Reinsch's test. One liter of the water is rendered slightly alkaline by sodium carbonate, free from arsenic, and evaporated nearly to dryness in a porcelain basin. 2 or 3 c. c. of water strongly acidulated with hydrochloric acid are placed in a small test-tube, about $\frac{1}{2}$ square centimeter of bright copper foil is added, and the liquid boiled gently for a few

moments. If the copper remains bright, showing that the reagents contain no arsenic, the water-residue is acidified with hydrochloric acid, added to the contents of the test-tube, and the liquid again boiled for several minutes. If arsenic be present, a steel-gray stain will appear on the copper. The slip is removed, washed with distilled water, *thoroughly* dried by pressure between filter paper, inserted into a narrow glass tube closed at one end, which has been previously dried by heating nearly to redness. The tube is gently heated at the point at which the copper rests; the arsenical deposit will sublime and collect on the cooler portion of the tube, in crystals which the microscope shows to be octahedral.

Since small amounts of arsenic frequently occur in reagents and in glass vessels, care must be taken to avoid such sources of error. Sodium carbonate solution may contain arsenic dissolved from the glass bottle in which it is kept. It is best, therefore, to use the solid carbonate for rendering the water alkaline, and to determine its freedom from arsenic before use.

Iron is detected by the addition of a drop of ammonium sulphide to the water in a tall glass cylinder. Ferrous sulphide is formed, having a greenish-black color, instantly discharged by acidifying the water with dilute hydrochloric acid. A still better test is the production of a blood-red color, with potassium sulphocyanate, due to the formation of ferric sulphocyanate. The water should be first boiled with a few drops of nitric acid, to convert the iron to the ferric condition, cooled, and a drop or two of the solution of potassium sulphocyanate added. The test is very delicate. Either of the above tests may be made quantitative

by matching the color produced in 100 c. c. of the water with that obtained from a known weight of iron. The method with potassium sulphocyanate is preferable, as it is more delicate and there are fewer interfering conditions. The following is the method as elaborated by Thompson and described in Sutton's "Volumetric Analysis:"—

Solutions Required:—

Standard Ferric Sulphate.—0.7 gram ferrous ammonium sulphate are dissolved in water acidified with sulphuric acid, and potassium permanganate solution added until the solution turns a very faint pink color. The solution is diluted to a liter. 1 c. c. contains 0.1 milligram iron.

Diluted Nitric Acid.—30 c. c. concentrated nitric acid diluted with water to about 100 c. c.

Potassium Sulphocyanate.—5 grams of the salt dissolved in about 100 c. c. water.

Analytical Process:—

About 100 c. c. of the water are evaporated to small bulk, acidified with hydrochloric acid, and just sufficient dilute potassium permanganate solution added to convert all the iron to the ferric condition. The liquid is evaporated nearly to dryness to drive off excess of acid, then diluted to its original volume, 100 c. c. In two tall glasses marked at 100 c. c., 5 c. c. of the nitric acid and fifteen c. c. of the sulphocyanate solution are placed. To one of these a measured volume of the treated water is added and both vessels filled up to the mark with distilled water. If iron is present, a blood-red color will be produced. Standard iron solution is added to the second vessel until the color agrees. The amount of water which is added to the first glass will depend upon the quantity of iron it contains ;

not more should be used than will require two or three c. c. of the standard to match it, otherwise the color will be too deep for comparison.

Manganese.—The following method is described by Wanklyn in his treatise on water analysis. About one liter of the water is evaporated to small bulk, nearly neutralized by hydrochloric acid and treated with a few drops of a solution of hydrogen dioxide. The formation of a brown precipitate indicates the presence of manganese. The test is very delicate. The precipitate may be collected on a filter, the filter ashed, and the residue fused with a mixture of sodium carbonate and potassium nitrate. Green potassium manganate will be produced, which, when boiled with water, will give a bright red solution of potassium permanganate. The quantitative determination is given elsewhere.

Lead may be readily detected by adding to the water in a tall glass cylinder a drop of ammonium sulphide; brownish black lead sulphide is formed, which does not dissolve either by acidulating the water with dilute hydrochloric acid (distinction from iron) nor by the addition of about one c. c. of a strong solution of potassium cyanide (distinction from copper). S. Harvey (*Analyst, April, 1890*) gives the following method for detecting lead in water: 250 c. c. are placed in a conical precipitating jar, about 0.1 gram of crystallized potassium dichromate is added and dissolved by agitation. The same volume of lead-free water is treated in the same manner, and the two solutions placed side by side. Water containing 0.3 parts per million, will show a turbidity in fifteen minutes, which will be rendered more distinct by contrast with the clear water alongside. By allowing the jar to stand for about twelve

hours undisturbed, the precipitate will settle and will become still more distinct. No other metal likely to be present in water will give a similar reaction.

In the absence of copper, the amount of lead present may be determined as follows: A solution is prepared containing 1.6 grams of lead nitrate to the liter; one c. c. of this contains one milligram lead. 100 c. c. of the water to be tested are placed in a tall glass vessel, made acid by the addition of a few drops of acetic acid and five c. c. of hydrogen sulphide added. In a similar vessel 100 c. c. of distilled water are placed, together with the same quantities of acetic acid and hydrogen sulphide, and sufficient of the standard lead solution to match the tint in the first cylinder. The amount of lead in the water under examination is thus known.

Copper is detected in the same manner as lead by acidifying the water with acetic acid and adding hydrogen sulphide water. The precipitate is distinguished from lead sulphide by the fact that the color is discharged on the addition of about one c. c. of a strong solution of pure potassium cyanide. It may be further confirmed by the addition to another portion of the water of a solution of potassium ferrocyanide. In the presence of even a very small amount of copper, a mahogany red color is produced.

In the absence of lead, copper is estimated in the same way as that metal, using, however, a standard solution of copper for the comparison liquid. This is made by dissolving 3.929 grams of crystallized copper sulphate in one liter of water. One c. c. of the solution contains one milligram copper.

If both lead and copper are present, a large quantity of the water should be evaporated to small bulk, and the

metals separated and estimated by any one of the ordinary laboratory methods.

The following table, prepared by A. J. Cooper, indicates the comparative delicacy of some of the ordinary tests for the detection of poisonous metals in water :—

| Metal. | Reagent. | Depth of Liquid, $3\frac{3}{4}$ inches. | Depth of Liquid, $14\frac{1}{2}$ inches. Cylinder enclosed in opaque tube. |
|---------------|-------------|---|---|
| | | 1 part of metal detected in | 1 part of metal detected in |
| Copper . . . | K_4Cy_6Fe | 4,000,000 of water. | 11,750,000 of water. |
| " . . . | NH_4HO | 1,000,000 " | 1,950,000 " |
| " . . . | H_2S | 4,150,000 " | 15,660,000 " |
| Zinc . . . | NH_4HS | 2,500,000 " | " |
| Arsenic . . . | H_2S | 3,600,000 " | 7,520,000 " |
| Lead . . . | K_2CrO_4 | 4,000,000 " | 5,875,000 " |
| " . . . | H_2S | 100,000,000 " | 196,000,000 " |

TECHNICAL EXAMINATIONS.

GENERAL QUANTITATIVE ANALYSIS.

Silica, Iron, Aluminum, Manganese, Calcium, and Magnesium.—One liter of the water acidified with hydrochloric acid is evaporated to complete dryness, best in a platinum dish, the residue treated with hydrochloric acid and water, and the separated *silica* filtered, washed, dried, ignited in a platinum crucible and weighed.

To the filtrate, previously boiled with a few drops of strong nitric acid, slight excess of ammonium hydroxide is added, the liquid boiled several minutes, the precipitate collected, washed thoroughly with boiling water, dried, ignited and weighed. It consists of Fe_2O_3 and Al_2O_3 . It also contains all the phosphates and some manganese if much is present in the water. In such cases the precipitate

before drying is re-dissolved in hydrochloric acid and neutralized with a dilute solution of ammonium carbonate until the water almost becomes turbid. It is then boiled and the precipitate, now free from manganese, washed, dried, ignited and weighed. The iron may be determined by dissolving the precipitate in strong hydrochloric acid and employing the colorimetric method described on page 50.

If no manganese or only traces are present, the filtrate from the iron is mixed with sufficient ammonium chloride to prevent the precipitation of the magnesium, ammonium hydroxide, and then ammonium oxalate added in quantity sufficient to precipitate the calcium and to convert all the magnesium into oxalate, and thus hold it in solution. The precipitate contains all the calcium and some of the magnesium. If the magnesium is present only in relatively small quantity the amount carried down may be disregarded; otherwise a second precipitation should be made as follows: The solution is allowed to stand until the precipitate has subsided; this will require some hours. The supernatant liquid is poured off through a filter, the precipitate washed by decantation, then dissolved in hydrochloric acid, water added, then ammonium hydroxide and a small quantity of ammonium oxalate. After the calcium oxalate has thoroughly subsided it is filtered off, washed and dried. If quite small in amount it is placed with the filter in a weighed platinum crucible, ignited over the Bunsen burner for a short time, and then over the blast lamp for from five to fifteen minutes. The calcium is thus obtained in the form of oxide, which is allowed to cool in the desiccator and weighed. The weight thus obtained multiplied by 0.7142 gives the weight of *calcium*. When the amount of precipi-

tate is large, it is better to remove it from the filter, and heat it just short of redness until it assumes a grayish tint. It then consists of calcium carbonate. To this is added the ash of the filter. The weight of the calcium carbonate multiplied by 0.4 gives the weight of calcium.

The filtrates are mixed, slightly acidified with hydrochloric acid, concentrated and cooled, ammonium hydroxide and sodium phosphate added in excess, stirred briskly and allowed to stand in the cold for about twelve hours. The precipitated ammonium magnesium phosphate is brought upon a filter, that adhering to the sides of the vessel being dislodged by rubbing with a glass rod tipped with a piece of clean rubber tubing. It is washed with a solution made by mixing one part of the ammonium hydroxide of 0.96 sp. gr. with three parts of water. The precipitate is dried, transferred to a platinum crucible, the filter ashed separately and added to it, and the whole heated at first gently and then to intense redness for several minutes. After cooling, it is weighed. It consists of magnesium pyrophosphate; the weight multiplied by 0.2162 gives the weight of *magnesium*.

Manganese, if present in appreciable quantity, is separated before the precipitation of the calcium, as follows: The filtrate from the iron precipitate is slightly acidulated with hydrochloric acid, concentrated, and the manganese precipitated as sulphide by colorless or slightly yellow solution of ammonium sulphide. The flask, which should be nearly full, is stoppered, allowed to rest in a moderately warm place until the precipitate has thoroughly settled, filtered, washed with dilute ammonium sulphide water and purified by dissolving in a small quantity of hydrochloric acid and reprecipitating with ammonium sulphide. It is

filtered off, washed as before, dried, placed in a weighed porcelain crucible, covered with a little sulphur and ignited in a current of hydrogen introduced into the crucible by a tube passing through a hole in the cover. The pure manganese sulphide thus obtained is allowed to cool and weighed. The weight multiplied by .63218 gives *manganese*.

Sulphates.—500 c. c. of the clear water are slightly acidulated with hydrochloric acid, heated to boiling, and barium chloride solution added in moderate excess. The precipitate is allowed to subside completely, collected upon a filter, washed thoroughly, dried and incinerated. It is BaSO_4 ; the weight multiplied by 0.412 gives SO_4 . If the proportion of SO_4 is very low, it will be advisable to concentrate the water to one-fifth or one-tenth its bulk before precipitating.

Control. Potassium, Sodium and Lithium.—From 250 to 1000 c. c. of the water, according to the amount of solid matters present, are evaporated to dryness in a platinum dish, and the residue heated in an air-bath to about 360°F. , until the weight becomes constant. This determines the total solid matter in solution.

The residue is treated with a small amount of water and sufficient dilute sulphuric acid to decompose the salts present. The dish should then be covered and placed upon the water-bath for five or ten minutes, after which any liquid spurted on the cover is washed into the dish, the whole evaporated to dryness and heated to redness. A few drops of ammonium carbonate solution should then be mixed with the residue, and the ignition repeated to insure the removal of the last portions of free acid. In the majority of cases the only basic elements present in considerable quantity

are calcium, magnesium and sodium. The *sodium* may be determined indirectly, therefore, by calculating from the amount of Ca and Mg found, the calcium and magnesium sulphate in the residue, and subtracting this sum, together with the silica, from the total residue.

If potassium or potassium and lithium, also, are to be estimated, the filtrate from the precipitation of the SO_4 may be used, provided that sufficient of the water has been used for the estimation. For the determination of potassium and sodium in ordinary well and river waters, not less than one liter should be employed. When lithium is to be determined, it is generally necessary to use at least two or three liters. In any case, as the alkalis are to be weighed as chlorides, it is advisable to precipitate the sulphates by addition of barium chloride. Unless the sulphates are to be estimated in this portion, it is unnecessary to remove the precipitate of barium sulphate so formed.

The water is evaporated to about 200 c. c., thin, pure milk of lime added in slight excess—generally from two to three c. c. will be sufficient—to the hot liquid, and the heat continued for several minutes. It is then washed into a 250 c. c. flask, disregarding the insoluble portion adhering to the dish, which, however, should be thoroughly washed, and the washings added to the flask. After cooling, the flask is filled up to the mark with distilled water, thoroughly mixed, the precipitate allowed to settle, and the liquid filtered through a dry filter. 200 c. c. of the filtrate are measured into another 250 c. c. flask, ammonium carbonate and ammonium oxalate added, filled with water up to the mark, mixed, allowed to settle, filtered through a dry filter, 200 c. c. of the filtrate measured off and evaporated to *thorough dryness* in a platinum crucible, heating very

cautiously at the last stages to avoid loss by spurting. The low-temperature burner is suited for this purpose. The crucible is now covered and cautiously heated to dull redness, cooled and weighed. The residue consists of potassium, lithium and sodium chlorides. It contains sometimes, also, traces of magnesium, which may be removed by treating again with lime and with ammonium carbonate and oxalate. It is frequently of advantage, in evaporating these saline solutions, to add, when the solution becomes concentrated, several c. c. of strong hydrochloric acid. This precipitates the greater portion of the salts in a finely granular condition, and renders loss by spurting less liable to occur.

If potassium and sodium chlorides only are present, they can be readily estimated by dissolving the weighed residue in water, determining the total chlorine by titration with silver nitrate and potassium chromate, and applying the following rule: "Multiply the quantity of chlorine in the mixture by 2.1035, deduct from the product the sum of the chlorides, and multiply the remainder by 3.6358; the product expresses the quantity of sodium chloride contained in the mixed chloride."

The results by this method are not accurate if either the potassium or the sodium is present in relatively small amount. In such cases the following procedure may be resorted to. The weighed chlorides are dissolved in a small quantity of water, an excess of a concentrated neutral solution of platinum chloride added, evaporated nearly to dryness at a low heat on the water bath, some 80 per cent. alcohol added, allowed to stand, the clear liquor decanted off on a small filter and the residue washed in this way several times by fresh small portions of 80 per cent. alcohol.

The precipitate is then washed on to the filter with alcohol, washed again with 80 per cent. alcohol, thoroughly dried and transferred as far as possible to a watch glass. The small portion on the filter is dissolved off and the solution placed in a weighed platinum dish and evaporated to dryness. The main portion on the watch glass is then added, and the whole dried to a constant weight at about 260° F., cooled and weighed. The weight thus found multiplied by .30557 gives the weight of *potassium chloride*. This subtracted from the combined weight of the chlorides gives the weight of *sodium chloride*.

Lithium, if present, is best separated before the treatment with platinum chloride. The following method, devised by Gooch, gives good results: To the concentrated solution of the weighed chlorides, amyl alcohol is added and heat applied, gently at first, to avoid bumping, until the water disappears from the solution and the point of ebullition becomes constant at a temperature which is approximately that at which the alcohol boils (270° F.), the potassium and sodium chlorides are deposited and the lithium chloride is dehydrated and taken into solution. The liquid is then cooled and a drop or two of strong hydrochloric acid added to reconvert traces of lithium hydroxide in the deposit, and the boiling continued until the alcohol is again free from water. If the amount of lithium chloride be small, it will be found in the solution and the potassium chloride and sodium chloride in the residue, excepting traces which can be allowed for. If the lithium chloride exceed ten or twenty milligrams the liquid may be decanted, the residue washed with amyl alcohol, dissolved in a few drops of water and treated as before. For washing, amyl alcohol previously dehydrated by boiling is to be

used, and the filtrates are to be measured apart from the washings. In filtering, the Gooch filter with asbestos felt may be used with advantage, applying gentle pressure by the aid of the filter pump. The crucible and residue are ready for weighing after gentle heating over the low-temperature burner. The weight of the insoluble chlorides is to be corrected by adding .00041 for every ten c. c. of amyl alcohol in the filtrate, exclusive of the washings, if only sodium chloride be present; .00051 for every ten c. c. if only potassium chloride, and .00092 in the presence of both these chlorides.

The filtrate and washings are evaporated to dryness in a platinum crucible heated with sulphuric acid, the excess driven off, and the residue ignited to fusion, cooled and weighed. From the weight is to be subtracted, for each ten c. c. of filtrate, .0005, .00059, or .00109, according as only sodium chloride, potassium chloride, or both were present in the original mixture.

Hydrogen Sulphide.—The following method is taken from Sutton's "Volumetric Analysis:"—

Reagents Required:—

Centinormal Iodine.—Dry, commercial iodine is intimately mixed with one-fourth its weight of pure potassium iodide and gently heated between two clock-glasses by resting the lower on a hot plate. The iodine sublimes in a perfectly pure condition. It is allowed to cool under the desiccator, 1.265 grams weighed out, together with 1.8 grams of pure potassium iodide, dissolved in about 50 c. c. of water and the solution made up exactly to a liter. The liquid must not be heated, and care should be taken that no iodine vapor is lost. One c. c. is equivalent to .00017 H_2S . The solution is best preserved in stoppered bottles,

which should be completely filled and kept in the dark. It will not even then keep very long, and should be standardized by titration with a weighed amount of pure sodium thiosulphate, which should be powdered previous to weighing, and pressed between filter paper to absorb any moisture. 50 c. c. of the iodine solution, when of full strength, will require 0.124 gram of sodium thiosulphate.

Starch Indicator.—See page 39.

Analytical Process:—

10 c. c., or any other necessary volume of the iodine solution, is measured into a 500 c. c. flask, and the water to be examined added until the color disappears. 5 c. c. of starch liquor are then added and the iodine solution run in until the blue color appears; the flask is then filled to the mark with distilled water. The respective volumes of iodine and starch solution, together with the added water, deducted from the 500 c. c. will show the volume of water actually titrated by iodine. A correction should be made as follows for the excess of iodine required to produce the blue color: 5 c. c. starch solution are made up with distilled water to 500 c. c., iodine run in until the color matches that in the test, and the volume of iodine solution so used subtracted from the figure obtained in the first titration.

Hardness. CO_3 in Normal Carbonates.—Waters containing considerable quantities of calcium and magnesium salts are said to be hard. Since the solution of calcium and magnesium carbonate in water depends partly upon the presence of carbon dioxide, boiling precipitates the greater portion of the carbonates, the result being to diminish the hardness, *i. e.*, soften the water. Magnesium and calcium sulphates and chlorides are not precipitated in this

way. Hardness, therefore, is divided into two classes, temporary and permanent, the former being that which may be removed by boiling. The process here described is due to Hehner.

Reagents Required :—

Standard Sodium Carbonate.—1.06 grams of recently ignited pure sodium carbonate are dissolved in water and the solution diluted to 1000 c. c. 1 c. c. = .00106 gram Na_2CO_3 , equivalent to .001 gram CaCO_3 .

Standard Sulphuric Acid.—1 c. c. of pure concentrated sulphuric acid is added to about 1000 c. c. of water. 50 c. c. of the standard sodium carbonate are placed in a porcelain dish, heated to boiling, a few drops of a solution of phenacetolin or lacmoid added, and the sulphuric acid cautiously run in from a burette until the proper change of color occurs. From the figure thus obtained, the extent to which the acid should be diluted in order to make 1 c. c. of the sodium carbonate equivalent to 1 c. c. of the acid may be calculated. The proper amount of water is then added and the solution verified by again titrating.

Analytical Process :—

Temporary Hardness.—100 c. c. to 250 c. c. of the water tinted with the indicator are heated to boiling, and the sulphuric acid cautiously run in until the color change occurs. Each c. c. required will represent one part of calcium carbonate or its equivalent per 100,000 parts of the water.

Permanent Hardness.—To 100 c. c. of the water is added an amount of the sodium carbonate solution more than sufficient to decompose the calcium and magnesium sulphates, chlorides and nitrates present; usually a bulk equal to the water taken will be more than sufficient. The mixture is evaporated to dryness in a nickel or platinum

dish, and the residue extracted with distilled water. The solution is filtered through a very small filter, and the filtrate and washings titrated hot with sulphuric acid as above ; or 25 c. c. of distilled water may be poured on the residue, and the solution obtained filtered through a dry filter, the filtrate measured and titrated. The difference between the number of c. c. of sodium carbonate used and the acid required for the residue will give the permanent hardness.

If the water contains sodium or potassium carbonate there will be no permanent hardness, and there will be more acid required for the filtrate than the equivalent of the sodium carbonate added. From this excess the quantity of sodium carbonate in the water may be determined.

Since any alkali carbonate in the water would be erroneously calculated as temporary hardness by the direct titration, the equivalent, in terms of calcium carbonate, of the alkali carbonate present should be deducted from the figure given by the titration in order to get the true temporary hardness.

The total CO_3 in normal carbonates is given by the direct titration of the water with dilute sulphuric acid. One c. c. of the acid is equivalent to .0006 gram of CO_3 .

Free Carbonic Acid.—The following process, due to Pettenkofer, is taken from Sutton's "Volumetric Analysis":—

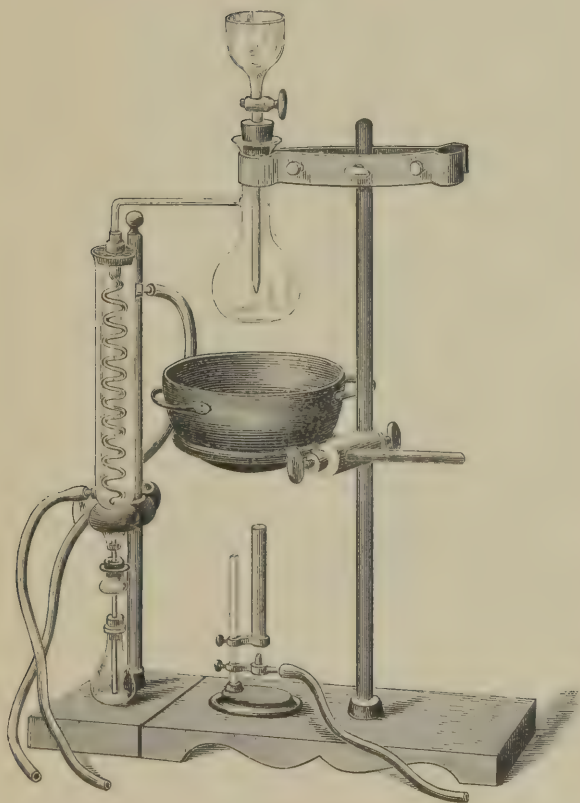
A stoppered bottle of known capacity, about 150 c. c., is filled at the source by submergence, or, if taken from a faucet, by allowing the stream to run in with full force for some minutes, the nozzle being inserted into the neck of the bottle. 50 c. c. of the water are then quickly removed

by a pipette, and the following solutions immediately added: 3 c. c. of a saturated solution of calcium chloride and 2 c. c. of a saturated solution of ammonium chloride; 45 c. c. of clear calcium hydroxide solution of known strength are added, the flask well corked, the liquids mixed, and set aside for at least twelve hours, to allow the calcium carbonate formed to settle and become crystalline and insoluble. An aliquot part (50 to 100 c. c.) of the clear liquid is then drawn off and titrated with decinormal acid, using phenacetolin or lacmoid as indicator, and from the amount required the entire proportion of calcium hydroxide unacted upon can be determined. This being deducted from the amount originally added, and the remainder multiplied by .0022, will give the weight of carbonic acid in the water in excess of that existing as normal carbonates.

Boric Acid.—*Detection.*—Add to one liter of the water sufficient sodium carbonate to render it distinctly alkaline. Evaporate to dryness, acidify with hydrochloric acid, moisten a slip of turmeric paper with the liquid, and dry it at a moderate heat. In the presence of boric acid the paper will assume a distinct brown-red tint.

Estimation.—The following method for determining boric acid is due to Gooch, and has been found very satisfactory. One liter or more of the water is rendered alkaline, if necessary, by sodium carbonate and evaporated to dryness. The residue is transferred as completely as possible by the aid of slight excess of acetic acid to a flask attached to a condensing apparatus, arranged as in Fig. 8. About 1 gram of pure quicklime is heated in a platinum crucible over the blast lamp for from five to fifteen minutes, to decompose any hydroxide or

FIG. 8.



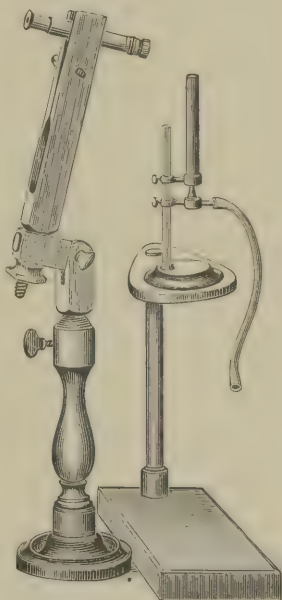
carbonate, allowed to cool in the desiccator, and weighed. It is then introduced into the Erlenmeyer flask, slaked by the addition of a few c. c. of water, and the flask attached to the lower end of the condenser, as shown (Fig. 8). The terminal tube of the condensing apparatus should dip into the milk of lime. The hemispherical copper basin contains paraffin, which is heated to a temperature of about 250° F. The bath is then raised so as to immerse the entire bulb of the flask, and the liquid distilled to dryness. The bath is then lowered, and when the flask and its contents have somewhat cooled, 10 c. c. of methyl alcohol are introduced by means of the stoppered funnel tube, the bath raised again, and the liquid again distilled to dryness. This manipulation is repeated until six portions of 10 c. c. of methyl alcohol have been distilled off. The boric acid will distill over and be fixed by the lime. The contents of the Erlenmeyer flask are concentrated and transferred completely to the same crucible in which the lime was heated. Any portions adhering to the sides of the flask or to the tube may be dissolved by a little acetic acid. The material in the crucible is cautiously dried and heated over the blast lamp for ten minutes, allowed to cool in the desiccator and weighed. The increase in weight represents boric anhydride, B_2O_3 .

SPECTROSCOPIC EXAMINATION.

For the ordinary spectroscopic examination of a water a simple apparatus will suffice. The arrangement figured in the cut (Fig. 9) is a small direct-vision spectroscope, held in a universal stand, with Turquem's adjustable burner as the source of heat. The entire apparatus does not cost over \$15.00, and will be found convenient and efficient.

For the examination, a liter or more should be evaporated nearly to dryness, a little hydrochloric acid being added near the end of the process, the residue placed in a narrow strip of platinum foil having the sides bent so as to retain the liquid, and heated in the flame. While this method will be sufficient in many cases, a far better plan is to separate the substance sought for in a state of approximate purity and then examine with the spectroscope. Very small traces of lithium, for instance, may be detected as follows: To about a liter of the water sufficient sodium carbonate is added to precipitate all the calcium and magnesium, and the liquid boiled down to about one-tenth its bulk; it is then filtered, the filtrate rendered slightly acid with hydrochloric acid and evaporated to dryness. The residue is boiled with a little alcohol, which will dissolve out the lithium chloride. The alcoholic solution is evaporated to dryness, the residue taken up with a little water and tested in the flame.

FIG. 9.



In order to identify with certainty any line which may be obtained, it is only necessary to hold in the flame at

the same time a wire which has been dipped in a solution of the substance supposed to be present, and to note whether the lines produced by it and the material under examination are identical.

SPECIFIC GRAVITY.

In the great majority of cases the determination of specific gravity is not essential. Ordinary river, spring and well waters contain such small proportions of solid matter that it is usually the practice to take a measured volume and to assume its weight to be that of an equal bulk of pure water. If the proportion of solids be high, a determination of the specific gravity may be desirable. For this purpose the specific gravity bottle may be used. This consists merely of a small flask provided with a finely perforated glass stopper. The bottle is weighed first alone, then filled with distilled water at 60° F., and finally with the water under examination at the same temperature. In filling the bottle, the liquid is first brought to the proper temperature, the bottle completely filled, the stopper inserted, and the excess of water, forced out through the perforation and around the sides of the stopper, carefully removed by bibulous paper. The weight of the water examined divided by the weight of the equal bulk of distilled water at the same temperature gives the specific gravity.

Another method, and one which gives very satisfactory results, is by the use of a plummet. This may conveniently consist of a piece of thick glass rod of about 10 c. c. in bulk, or of a test-tube weighted with mercury and the open end sealed in the flame. The plummet is suspended to the hook of the balance by means of a fine platinum wire and

its weight ascertained. It is then immersed in distilled water at 60° F. and the loss in weight noted. The figure so obtained is the weight of a bulk of water equal to that of the plummet. This having been determined, the specific gravity of any water may be found by immersing in it the plummet and noting the loss in weight. This, divided by the loss suffered in pure water, gives the specific gravity.

INTERPRETATION OF RESULTS.

STATEMENT OF ANALYSIS.

The composition of water is generally expressed in terms of a unit of weight in a definite volume of liquid, but much difference exists as to the standard used. The decimal system is very largely employed, the proportions being expressed in milligrams per liter, nominally parts per million; or in centigrams per liter, nominally parts per hundred thousand. Not infrequently the figures are given in grains per imperial gallon of 70,000 grains, or the U. S. gallon of 58,328 grains. Much more rarely grains per quart, parts per thousand, per cent. or other inconvenient ratios are employed. In this work the composition is always expressed in parts per million. This ratio is practically equivalent to milligrams per liter, except in cases of waters very rich in solids, a liter of which weighs notably more than one million milligrams. Factors for converting the different ratios are given at the end of the book.

From the analysis of a water it is rarely possible to ascertain the exact arrangement of the elements determined, but it is the custom to assume arrangements based upon the rule of associating in combination elements having the highest affinities, modifying this system by any inferences derived from the character or reactions of the water itself. It has been demonstrated that, even in the case of mixtures of salts producing no insoluble substances, partial inter-

change of the basylous and acidulous radicles takes place. In a solution of sodium chloride and potassium sulphate, sodium sulphate and potassium chloride will be found, as well as the original salts. When the conditions are rendered more complex by the addition of other substances, it is obviously impossible to determine the exact arrangement. In view of these facts, it is preferable to express the composition of a water by the proportion of each element or radicle present. In this way a water containing K_2SO_4 , will be expressed in terms of K and SO_4 , respectively. In the case of bodies like CO_2 and SiO_2 , which may possibly exist free in the water, their proportion is expressed as such. It frequently occurs that the characteristics of some of the compounds in a water are sufficiently marked to indicate their presence, and there can be no objection to suggesting in connection with the analytical statement, the inferences which may thus be drawn.

The organic matter, or its derived products, are best stated in terms of the nitrogen which they contain, thus permitting a comparison of the different stages of decomposition. It is inadvisable to represent the amount of unchanged organic matter in terms of oxalic acid, as has been suggested, or to express the nitrogen in terms of albumin, or any other supposititious compound.

SANITARY APPLICATIONS.

Judgment upon the analytical results from a given sample of water depends upon the class to which it belongs, and to the particular influences to which it has been subjected. A proportion of total solids which would be suspicious in a rain or river water, would be without significance in that from an artesian well. On the other hand, a

subsoil water of unobjectionable character would contain a proportion of nitrates which would be inadmissible in the case of a river or deep water. Location has also much bearing in the case; subsoil waters near the sea will be found to contain, without invoking suspicion, proportions of chlorine which would be ample to condemn the same sample if derived from a point far inland. Hence the importance of recording at the time of collection, all ascertainable information as to the surroundings and probable source of the water.

Color, Odor and Taste.—Water of the highest purity will be clear, colorless, odorless, and nearly tasteless. While in some cases a decided departure from this standard may give rise to suspicion, analytical observations are necessary to decide the point. Water highly charged with mineral matters will possess decided taste, vegetable matters may communicate distinct color; but, on the other hand, it may be highly contaminated with dangerous substances and give no indications to the senses. Well-waters occasionally become offensive in odor, from penetration of tree roots. The odor often recalls that of hydrogen sulphide. Sulphides are, indeed, often formed in such cases by the abstraction of oxygen from sulphates under the influence of microbes. Such waters are often used without apparent injury, but it is probable that if direct pollution occurs, the danger would be enhanced by the presence of the vegetable matter. Miquel has described a bacillus, under the name *B. sulphhydrogenus*, which produces hydrogen sulphide readily. Some of the common putrefactive bacilli doubtless have this power also, largely through the influence of the hydrogen liberated by them. In waters containing hydrogen sulphide, species of beg-

giatoa, especially *B. alba*, thrive, and decomposing the sulphide, become impregnated with sulphur. Natural sulphur waters frequently contain these organisms, as do, also, waste-waters containing sulphide.

Total Solids.—Excessive proportions of mineral solids, especially of marked physiological action, are known to render water non-potable, but no absolute maximum or minimum can be assigned as the limit of safety. Distilled water and waters very highly charged with mineral matter have been used for long periods without ill effects. The popular notion that the so-called hard waters conduce to the formation of urinary calculi is not borne out by surgical experience nor statistical inquiry. Many urinary calculi are composed of uric acid, and are the results of disorders of the general nutritive functions.

Sanitary authorities have fixed an arbitrary limit of total solids of about six hundred parts per million, but many artesian waters in constant use exceed this. An instance is found in the well on Black's Island, near Philadelphia, given in the table of analyses, which contains nearly twelve hundred parts per million, is very agreeable in taste, and has been in constant use for some years by a number of persons without injury. The assertion that water to be wholesome must contain an appreciable proportion of total solids is also not demonstrated by clinical experience. A discussion of the effects of special mineral ingredients, *e. g.*, magnesium sulphate, ferrous carbonate, etc., belongs to general therapeutics.

The odor produced on heating the water residue is often of much use in detecting contamination. Odors similar to those produced by heating glue, hair, rancid fats, urine, or other animal products, will give rise to grave suspicion.

On the other hand, a more favorable judgment may be given when the odor recalls those given off in the heating of non-nitrogenized vegetable materials, such as wood-fibre.

Poisonous Metals.—The proportion of iron in water constantly used for drinking purposes should not much exceed three parts per million. Lead, copper, arsenic and zinc must be considered dangerous in any amount, though it appears that zinc and copper, being least cumulative, are rather less objectionable in minute amount than the others. Concerning the limit of safety with manganese and chromium very little is known, but their presence in appreciable quantity must be looked upon with suspicion.

Chlorides and Phosphates.—Chlorides—principally sodium chloride—and phosphates are abundantly distributed in rocks and soils, and find their way into natural waters ; but while the former are freely soluble, and remain in undiminished amount under all conditions to which the water is subjected, all but minute amounts of the latter are either precipitated or removed by the action of living organisms. Surface and subsoil waters ordinarily contain but a few parts per million. Both chlorides and phosphates being constant and characteristic ingredients of animal excretions, it is obvious that an excess of them in natural waters, unless otherwise accounted for, will suggest direct contamination. Proximity to localities in which sodium chloride is abundant, such as the sea or salt deposits, will deprive the figure for the chlorine of diagnostic value, nor can any indication of sewage or other dangerous pollution be inferred from high proportion of chlorine in deep waters. Further, it has been shown that the pro-

portion of chlorine in uncontaminated waters is tolerably constant, while in water subjected to the infiltration of sewage, the chlorine undergoes marked variation in amount. In most cases, therefore, a correct judgment can only be attained by comparison with the average character of the waters of the same type in the district, and by examination at intervals of the water in question.

As regards phosphates, Hehner, who has published a series of analyses, states that the presence of more than 0.6 parts per million—calculated as PO_4 —should be regarded with suspicion. On the other hand, the absence of phosphates affords no positive proof of the freedom from pollution. The application of Heisch's test will often afford additional information on this point. F. E. Lott, who has applied this test in the examination of a number of waters, fully confirms Dr. Frankland's statement that the development is due to phosphates, and draws the following conclusions:—

Any water which undergoes butyric fermentation when simply treated with cane sugar and kept at a temperature of 80°F. , may be at once condemned as unfit for domestic use.

The single fact of a water not undergoing butyric fermentation is no proof of its purity.

A water which remains clear under this treatment would certainly be less likely to be contaminated by sewage than one which becomes milky, and the possibility of unoxidized sewage matter being in a water which remains quite clear is very doubtful.

The butyric ferment is not perceptibly influenced by the presence of abnormal amounts of chlorine, ammonia, nitrogenous matter, sulphates or nitrates, but is a very accurate indicator of the presence of phosphates.

Nitrogen from Ammonium Compounds.—Ammonium compounds are usually the results of the putrefactive fermentation of nitrogenous organic matter ; they may also be the product of the reduction of nitrites and nitrates in presence of excess of organic matter. In either case, therefore, they suggest contamination. Deep waters often contain an excess of ammonium compounds, derived, in large part, from the reduction of nitrates. Their presence here is hardly ground for adverse judgment, since the water, even though originally contaminated, has undergone extensive filtration and oxidation and its organic matter converted into bodies presumably harmless. Such waters, indeed, usually show only traces of unchanged organic matter.

Rain water often contains large proportions of ammonium compounds ; but here, also, the fact cannot condemn the water, since it does not indicate contamination with dangerous organic matter.

The evolution of ammonia in the distillation of rain water often continues indefinitely, the larger portion passing over in the first distillates, but small quantities being present even after the distillation has been much prolonged. The same continuous evolution of ammonia is noted in waters containing urea, but in this case a larger proportion is collected in the earlier distillates, nearly all coming over before one-half the water has been distilled. Fox gives the following figures as ratios obtained in the analysis of two samples, one of rain water collected from a roof and therefore impure, and the other of a water containing urine :—

| RAIN WATER. | | URINE WATER. | | | |
|-------------------------|-----|--------------|------|--------------------|--|
| 1st distillate, | .35 | .38 | | parts per million. | |
| 2d " | .25 | .14 | | " " | |
| 3d " | .12 | .065 | | " " | |
| 4th " | .09 | .035 | | " " | |
| 5th " | .09 | . . | | " " | |
| 6th " | .04 | . . | | " " | |
| 7th " | .03 | . . | | " " | |
| <hr/> | | <hr/> | | | |
| | | .97 | .620 | | |

Nitrogen by Alkaline Permanganate (Nitrogen of "albuminoid ammonia").—A large yield of ammonia by boiling with alkaline potassium permanganate will, of course, point to an excess of nitrogenous organic matter. The inferences to be drawn depend upon the origin and condition of the organic material. If animal, the water may at once be condemned as unsafe. Waters containing excessive amounts even of vegetable matter are not free from objection, since they have frequently caused persistent diarrhœa. If the organic matter, whether animal or vegetable, is in a state of active decomposition, it is doubly objectionable. Mallet has called attention to the fact that such waters, as a rule, yield ammonia rapidly, whereas non-decomposing material yields it but slowly, and he points out the importance, therefore, of noting the rate at which the ammonia collects in the distillate.

Dr. Smart has observed that water containing fermenting vegetable matter is colored yellow by boiling with sodium carbonate, and that when Nessler's reagent is added to the distillate, a greenish, in place of the ordinary yellowish-brown color is produced. He applies this fact in conjunction with the determination of the oxygen-consuming

power (Tidy's process) and the rate of evolution of the ammonia by alkaline permanganate as follows:—

A water yielding ammonia slowly by alkaline permanganate, contains recent organic matter; of animal derivation, if the oxygen-consuming power is low; of vegetable, if high.

A water yielding ammonia more rapidly by alkaline permanganate, shows decomposing organic matter; of animal origin, if the oxygen-consuming power be low and there be no interference with the Nessler reaction; of vegetable origin, if the oxygen consumed be high, and if a yellow color be produced in the water by sodium carbonate, and a greenish color in the nesslerized distillate.

Inferences as to the source of the organic matter can usually be drawn from the amount of chlorine and nitrates present. If the chlorine be high *i. e.*, in excess of the average of the district, it may be inferred that the material is, in great part, of animal origin. In this case, the nitrates will either be high or entirely absent, according as the contaminating matter has passed through soil or enters the water directly.

A large amount of vegetable matter will, as a rule, show itself by the color it imparts to the water.

Wanklyn gives the following standards:—

High purity,00 to .041 per million.

Satisfactory purity,041 to .082 “ “

Impure, over .082.

In the absence of ammonium compounds, he does not condemn a water unless the nitrogen by permanganate exceeds .081 per million; but a water yielding 0.123 parts per million of nitrogen by permanganate he condemns under all circumstances.

Total Nitrogen.—Drown and Martin's results with surface waters indicate that the total nitrogen obtained by their process is about twice that obtained by alkaline permanganate. Our own experiments accord with this. Further observation on different waters and by different observers will be required to determine the value to be assigned to the figures obtained by this method. This method is especially suitable for studying the effects of filtration, storage, etc., on the nitrogenous organic matter in water.

Nitrogen as Nitrites.—Nitrites are present in water as the result either of incomplete nitrification of ammonia, or the reduction of already formed nitrates, under the influence of reducing agents or microbes. Since they are transition products, their presence in water is usually evidence of existing fermentative changes, and, further, may be taken as indicating that the water is unable to dispose of the organic contamination. When, however, the conditions are such that oxidation cannot take place, nitrites may persist for a long time. This sometimes occurs in deep waters in which fermentative changes have long since ceased, but oxygen is not available. These contain not infrequently small amounts of nitrites, to which the same degree of suspicion cannot be attached. When nitrites are found in these waters, the possibility of their introduction from polluted subsoil water, through defective tubing, must not be overlooked. Rain water, also, sometimes contains nitrites derived from the air, and therefore not indicative of any putrefactive change. The presence of measurable quantities of nitrites in river or subsoil water is sufficient ground for condemnation.

Nitrogen as Nitrates.—Nitrates are the final point in the oxidation of nitrogenous organic matter, especially

animal matters. Rain water and that from mountain streams and deep wells, except from cretaceous strata, generally contain only traces, but river and subsoil waters will always contain appreciable amounts, unless some reducing action, such as recent sewage pollution, is at work. When, therefore, a water contains enough mineral matter to demonstrate its percolation through soil, and at the same time is free from nitrates or contains only traces, the occurrence of a destructive fermentation may be inferred. These cases are not uncommon among well waters, and the samples are generally turbid from suspended organic matter. Decided departure, either by increase or decrease, from the proportion of nitrates usual in the same class of water in any district may be taken as evidence of contamination.

Oxygen-consuming Power.—Sanitary authorities differ very much as to the significance of this datum. Attempts have been made to fix maximum limits for the various types of water, and also to gauge the character and condition of the organic matter by observing the rate at which the oxidation takes place, but no positive conclusions can be given. In general, it may be said that a sample which has high oxygen-consuming power will be more likely to be unwholesome than one which is low in this respect; but the interferences are so numerous, and the susceptibility to oxidation of different organic matters of even the same type, is so different, that the method is at best only of accessory value. It is especially suitable for consecutive determinations on the same supply.

The following proportions are given by Frankland and Tidy as the basis of interpreting the results of this method:—

| OXYGEN ABSORBED IN THREE HOURS. | | |
|---------------------------------|------------|--------------------|
| High organic purity, | .05 | parts per million. |
| Medium purity, | 0.5 to 1.5 | " " " |
| Doubtful, | 1.5 to 2.1 | " " " |
| Impure, | over 2.1 | " " " |

For the method with acidified permanganate at the boiling heat, the German chemists, who employ it largely, regard an absorption of 2.5 parts of oxygen per million as suspicious, and some sanitary authorities have fixed 3.8 parts of oxygen per million as the highest permissible limit.

Dissolved Oxygen.—Full aëration of water is favorable to the destruction of organic matter; a decided diminution in the quantity of dissolved oxygen may show excess of such matter and of microbic life. Gérardin has pointed out that this diminution is associated with the development of low forms of vegetable life, and Leeds has recorded similar facts. These changes are more likely to take place in still waters, and are frequently accompanied by disagreeable odor and taste. In cases in which stored waters become unpalatable, these facts should be borne in mind.

Dupré has given the following as the basis for interpreting the results of his adaptation of the determination of dissolved oxygen:—

“A water which does not diminish in its degree of aëration during a given period, may or may not contain organic matter, but presumably does not contain growing organisms. Such organic matter as it may be found to contain by chemical analysis need not be considered as dangerous impurity.”

“A water which by itself, or after the addition of gelatin or other appropriate cultivating matter, consumes oxygen from the dissolved air, at lower temperatures, but

does not consume any after heating for, say, three hours at 140° F., may be regarded as having contained living organisms, but none of a kind able to survive exposure to that temperature."

"A water which by itself, or after addition of gelatin or the like, continues to absorb oxygen from the contained air after heating to 140° F., may be taken as containing spores or germs able to survive that temperature."

Hardness.—The degree of hardness has but little bearing on the sanitary value of water, but is important in reference to its use for general household purposes, in view of the soap-destroying power which hard waters possess.

USUAL ANALYTICAL RESULTS FROM UNCONTAMINATED WATERS.

Parts per million.

| | Rain. | Surface. | Subsoil. | Deep. |
|-------------------------------------|----------------|-------------|------------|--------------------------|
| Total solids, | 5 to 20 | 15 upward | 30 upward | 45 upward |
| Chlorine, | Traces to 1 | 1 to 10 | 2 to 12 | Traces to large quantity |
| Nitrogen by permanganate, | .08 to .20 | .05 to .15 | .05 to .10 | .03 to .10 |
| " as NH_4 , | .20 to .50 | .00 to .03 | .00 to .03 | Generally high |
| " " nitrites, | None or traces | None | None | None or traces |
| " " nitrates, | Traces. | .75 to 1.25 | 1.5 to 5 | .00 to 3 |

ACTION OF WATER ON LEAD.

The almost universal use of lead pipes for conveying water, and the facility with which some waters corrode and dissolve the metal, make it a question of moment to determine the cause of this action and to devise means for its prevention. The subject has received considerable attention within the last few years, and the conditions which determine corrosion are now fairly understood. As a rule, it is found that waters free from mineral matter dissolve lead with facility, especially in the presence of oxygen. Some very soft waters are entirely without action, and this was unexplained until a few years ago, when Messrs. Crookes, Odling and Tidy found that the action was controlled by the amount of silica contained in the water. They found that those soft waters which, when taken from the service pipes, contained a notable quantity of lead, gave, on the average, three parts of silica per million; in those in which there was no lead, the silica present amounted to 7.5 per million and in those in which the action was intermediate, 5.5 parts per million. That it was really the silica that conditioned the corrosion, was confirmed by laboratory experiments. They also found that the most effective way of silicating a water is by passing it over a mixture of flint and limestone. The reason for this was pointed out later by Messrs. Carnelly and Frew, who showed that while calcium carbonate and silica both exert a protective influence, calcium silicate is more effective than either, and further, that in almost all cases in which corrosion took place it was greater in the presence of oxygen. This is particularly the case with potassium and ammonium nitrates and with calcium hydroxide. The

reverse is true of calcium sulphate, which is more corrosive when air is excluded. Their experiments also show that the presence of calcium carbonate or calcium silicate, altogether prevents corrosion by potassium and ammonium nitrates.

As the result of an elaborate series of experiments, Müller concludes, that while chlorides, nitrates and sulphates all act upon lead pipes, no corrosion takes place in the presence of sodium acid carbonate, and that calcium carbonate, by taking up carbonic acid, acts in the same way. This latter conclusion is at variance with the observations of Carnelly and Frew, who found that calcium carbonate is equally effective when carbonic acid is excluded. Müller also states that surface waters, contaminated by sewage and containing large amounts of ammoniacal compounds, will dissolve lead under all circumstances.

Allen has shown that water containing free acid, including sulphuric acid, acts energetically upon lead. This is not surprising in view of the later experiments, which prove that even calcium sulphate is corrosive. Later, W. Carleton-Williams found that even in the presence of free acid, corrosion may be prevented by the addition of sufficient silica. His experiments also confirm the view generally held, that soluble phosphates protect lead to a marked degree.

The following is a summary of the more important observations on this subject:—

Corrosive: Free acid or alkalis, oxygen, nitrates, particularly potassium and ammonium nitrates, chlorides and sulphates.

Non-corrosive and preventing corrosion by the above: Calcium carbonate, sodium acid carbonate, ammonium carbonate, calcium silicate, silica and soluble phosphates.

BIOLOGICAL EXAMINATIONS.

In a comprehensive sense the living organisms of water include representatives of all the great groups of animals and plants. The presence of any of the higher orders of organic forms may be taken as an indication of moderate purity, as these are absent from very foul water. From an analytical point of view, observation is limited to the determinations of those forms which are inappreciable to the unassisted eye. As far as regards some of the moderately complex organisms, such as the minute crustaceans, algæ, desmids, and even the amœbæ, it may be said that while some general inferences as to the character and history of the water may be deduced from an identification of the specific forms, no definite sanitary signification can be attached to them. The ova of the entozoa might in some cases be detected by careful search, and would indicate recent pollution of a highly dangerous character.

Cohn (*Beitr. z. Biol. d. Pflanz.*) regards chlorophyll-producing plants (diatoms and green algæ), together with the infusoria that feed upon them, and species of entomostrea (*Daphnia* and *Cyclops*), when present in only moderate amounts, as indicating water not very rich in dissolved organic matter. Species of *Cladothrix*, *Crenothrix* and *Beggiatoa*, which are among the larger bacteria, and frequently appear as branching forms, indicate suspended organic matter; while dissolved organic matter in a state of active decomposition is indicated by the presence of ordinary bacteria (*Bacilli*, *Spirilli*), etc.

Cladothrix dichotoma withdraws iron from water, and fixes it, causing obstructions in iron water pipes. *Crenothrix Kühniana*, Rabenhorst, is seen in water containing iron and sometimes causes a disagreeable odor.

The number of the higher forms present in any sample will depend very much upon the point at which it is collected, they being more numerous in the neighborhood of large plants and at the bottom and sides of streams. Under our present knowledge, no pathogenic power can be assigned to the higher forms of organic life, except entozoa, but their bodies after death may indirectly contribute to the rapid increase of the bacilli proper, by serving as food.

Instances of the introduction of the ova of entozoa into the human system by means of water are doubtless very common, and cases have been reported. One of the most striking of these was the anæmia occurring among the workmen in the St. Gothard tunnel, which was found to be due to the ingestion of the ova of a parasitic animal, *An-*

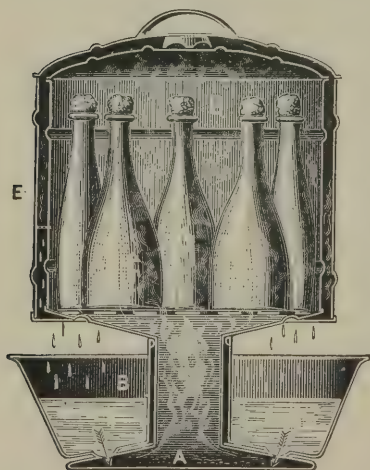
chylostomum duodenale.

Culture Media.—

For bacteriological examinations, culture media prepared with gelatine or agar-agar, are generally used. In special cases potatoes and blood-serum are employed. In all cases solutions and vessels must be thoroughly sterilized. This is most easily accomplished in the Arnold steam sterilizer, shown in Fig. 10.

It consists of a copper

FIG. 10.



boiler, A, in the form of an inverted funnel, which com-

municates with the sterilizing chamber. A double casing is so arranged that the condensed steam falls into the pan B and returns to the boiler. This pan should be about half-filled with water before starting. We have found this apparatus suitable not only for all sterilizations, but also for preparing solutions and for hot filtrations.

Meat-extract-peptone-gelatin :—

| | |
|------------------------------------|-----------|
| Water, | 1000 c.c. |
| Meat extract (Armour's), | 5 grams |
| Gelatin (best French), | 150 " |
| Peptone (Merck's, dry), | 10 " |
| Glucose (best), | 2 " |

The materials are dissolved by heat and the solution rendered slightly alkaline by the addition of sodium carbonate or trisodium phosphate, added by small portions, stirring between each addition, and testing the liquid by placing a drop of it on red litmus paper. When the alkaline reaction appears, the liquid is filtered through good filter paper, the funnel and beaker being placed in the sterilizer, and a gentle steaming maintained in order to keep the gelatin liquid.

In place of meat extract, a solution may be made as follows: macerate 500 grams of finely minced lean meat in 1000 c.c. of water, for twenty-four hours, at a temperature not over 45° F. Strain the liquid, add five grams of common salt and the peptone, gelatin and glucose, and render feebly alkaline, as before.

Agar-agar Mixture.—When cultures are to be conducted at a temperature above 68° F., agar-agar must be used as gelatinizing ingredient. The solution is prepared as given above, except that only 15 grams of agar-agar must be

used and a much longer time will be required for its solution. The operation can be facilitated by soaking the agar-agar for twelve hours in a strong solution of common salt, or by the following treatment, which was first described by Macé :—

20 grams of agar-agar, cut fine, are steeped in 500 c.c. of water, containing six per cent. of hydrochloric acid, with occasional stirring. It is then well washed, and placed for a similar period in the same amount of water, to which six per cent. of ammonium hydroxide has been added. It is again washed thoroughly and added to 1000 c.c. of boiling water. It dissolves at once. The peptone, gelatin and salt can then be added, the mixture rendered feebly alkaline and filtered in the sterilizer.

Agar-agar Gelatin.—To secure the advantages of both agar-agar and gelatin, a solution may be made by dissolving 50 grams of gelatin and 7.5 grams of agar-agar in a liter of water, adding the peptone, etc. in the usual proportions, rendering alkaline, filtering and sterilizing. The proportions of agar-agar and gelatin must be adhered to closely or the gelatinization may be lumpy and incomplete.

Potato Culture.—Cultivation on potatoes is an important method of distinguishing the *Bacillus typhosus*. Large, sound potatoes should be selected, thoroughly washed, and cut into disks about 5 cm. in diameter and 1 cm. thick. These are placed in glass boxes (pomade boxes) which have lids with ground joint, and heated for about one-half hour in the sterilizer. Another method is to cut out cylinders with the aid of an apple-corer, or largest size cork-borer, slice these obliquely, and place them in test-tubes, which are then closed with cotton plugs, and sterilized. The latter method does not give a large sur-

face, but the growth of any inoculation may be easily watched.

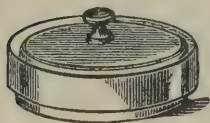
Collection of Samples.—Bacteriological examinations are of little value unless promptly made on samples that have been collected with precautions against contamination. The inoculation of the culture medium is best done at the source. If this is not possible, glass stoppered bottles holding about 200 c.c., which have been thoroughly sterilized, with stoppers in place, in a hot air oven at 300° F., must be used for collection. They should be rinsed on the *outside* with water, dipped below the surface, the stopper withdrawn, and again inserted when the bottle is full. If these are to be transported any distance they should be packed in ice. For delivering the measured volume of water, a pipette sterilized in the hot-air oven should be used.

Culture Manipulations.—For the estimation and isolation of microbes in water, we may employ either the original plate culture of Koch, Esmarch's "roll culture," or a modification that we have used in our own work, which may be designated "bottle culture."

Plate Culture.—Test-tubes containing about ten c.c. of nutrient jelly are plugged with cotton and steamed for fifteen minutes in the sterilizer on two successive days. In filling the tubes, care must be taken that none of the jelly touches the upper part, where it can come in contact with the cotton plug. After sterilization, the tubes should be put aside for a few days, to determine if all spores are destroyed. If no development of microbes takes place in this time, the jelly is ready for use. It should be melted at a low temperature in a water-bath, the cotton plug removed with a twisting motion and a measured volume of

water introduced by means of a sterilized pipette. The plug is immediately replaced and the liquids mixed by shaking, taking care not to soil the cotton. The quantity of water to be added will depend on the number of microbes supposed to be present. If the amount is probably quite small, 1 c. c. should be taken; if it is probable that a large number is present, 1 c. c. of the sample should be diluted to 10 c.c. with sterilized water, and 1 c.c. of this mixture used. In most cases it will be well to make several cultures, using different proportions of water. After the jelly and water have been mixed the liquid is poured out on a glass plate and allowed to set. The principal difficulty in the method arises from the liability to contamination from the air during this part of the process. The glass plates should, of course, be thoroughly sterilized.

FIG. 11.



They are usually set upon glass benches, and placed in a so-called moist chamber, which consists of two cylindrical glass dishes, one fitting within the other (Fig. 11). The benches and plates are placed in the inner dish. To hasten the setting of the jelly, it is necessary that the plates should be cold, and it will be best to have them resting in a level position on a flat tin bottle filled with ice water, or, if ice is not at hand, a recently prepared mixture of one part of ammonium nitrate with two parts of water. The coated plates must be protected from dust while being cooled, and as soon as possible must be transferred to the moist chamber, which, as well as the benches, should have been previously thoroughly washed with recently boiled water. The bottom should be covered with a sheet of moist filter paper. The plates

are kept in the chamber for several days. Each living microbe that is capable of growing in the jelly will become the centre of a colony of its own kind, which will soon become visible to the naked eye. The number of colonies may be counted as soon as they are distinct. When the number is very large, an approximate counting may be made by means of a glass plate with lines ruled so as to divide it into a considerable number of equal squares. This is placed over the culture, and the number of colonies in several of the squares counted, the result averaged and multiplied by the number of squares that the entire culture covers.

Roll Culture.—Instead of pouring the jelly on a plate, it may be spread in a uniform layer on the inner wall of the test-tube, taking care not to allow it to touch the cotton. The jelly may be rapidly hardened by rolling the tube in contact with ice. The method avoids all danger of contamination with dust and is very simple in manipulation, but is open to the objection that when bacilli are present which liquefy the gelatine, as will generally be the case, the fluid will run down and inoculate other portions of the layer.

Bottle Culture.—To avoid the disadvantage of the above methods, it will be found convenient to employ flat rectangular bottles of the form known technically as the "Blake" Bottle. Those of 8 or 10 ounce capacity are the best, and it is well to select such as have as uniform a thickness of glass as possible. They should be thoroughly cleaned and sufficient of the jelly put in to form a thin layer on one of the broader sides when the bottle is placed horizontally. The mouth is then closed by a cotton-plug and the bottle sterilized as described in connection with plate culture. To make a culture, the jelly is melted at a

low temperature, the measured volume of water added, the cotton plug replaced, and after mixing, the bottle is placed in a horizontal position for the usual time.

General Character of the Microbes in Natural Waters.—The microörganisms of natural waters are principally included in the genera *bacillus* and *spirillum*, especially the former. Micrococci and moulds are rare, and when they appear on the culture plate, are generally due to contamination by dust.

Microbes are distinguished according to the conditions favorable to their growth, as follows :—

Saprophytic. Growing on dead matter.

Parasitic. Growing only on living matter.

Aërobic. Requiring free oxygen.

Anaërobic. Not requiring free oxygen.

When the organism possesses the power of adapting itself to different conditions, the term *facultative* is applied ; when it can grow only under special conditions, the term *obligatory* is applied.

Thus, the *Bacillus butyricus* is unable to develop in contact with free oxygen ; it is an obligatory anaërobe. The *B. typhosus* can grow either on dead or living matter, and though growing best in presence of free oxygen, can also grow in the absence of it. It is, therefore, a facultative saprophyte, and a facultative anaërobe.

Microbes are also differentiated by the effect which they produce upon the culture medium. Some species rapidly or slowly liquefy the jelly with evolution of foul smelling gases ; others—chromogenic microbes—produce characteristic colors. Many do not produce any positive modification, and for purposes of distinction it is usual to transfer portions of the colonies to other culture media. Thus the

B. typhosus causes neither liquefaction nor coloration, but gives a distinct growth on potato. Such special cultures are obtained by taking up a portion of the colony on the end of a wire which has been just sterilized by heating to redness, and inoculating the prepared medium.

Cultivation in Absence of Oxygen.—Several of the most frequently occurring microbes are obligatory anaërobes, and will grow, therefore, only in an atmosphere deprived of free oxygen. Carbon dioxide has been found to act unfavorably upon their development. The most suitable atmosphere is one of pure hydrogen. Cultivation in such an atmosphere may be secured by constructing the moist chamber so as to permit its being filled with hydrogen and sealed, or by the use of Liborius' tube, Fig. 12.

The tube is charged with nutrient jelly, plugged with cotton, sterilized, inoculated with the material to be tested, the jelly maintained in a liquid condition by a very gentle heat and a current of pure hydrogen passed through the side tube until all air is expelled. The test-tube and side tube are then sealed quickly at the narrow portions, in the blow-pipe flame, and the jelly allowed to solidify.

FIG. 12.



Staining.—The differentiation of the various species of microbes may also be accomplished by staining with various aniline colors. These methods are, however, more generally applicable to pathological work, that is, to the staining of microbes in tissues; but one of the methods is here described, as it is frequently referred to in bacteriological literature.

Gram's Method of Staining (as given by Crookshank).—Place a few drops of pure aniline in a test-tube three-fourths full of water, and shake thoroughly. Filter the emulsion twice, collect some of the perfectly clear filtrate in a watch-glass and add, drop by drop, a concentrated alcoholic solution of gentian violet, until precipitation appears. Stain sections in this for about twenty minutes, then place them in a solution prepared as follows:—

| | |
|-----------------------------|-------------|
| Iodine, | 0.1 gram |
| Potassium iodide, | 0.2 “ |
| Water, | 30.0 grams. |

Allow them to remain until dark brown. Decolorize by placing in alcohol. This process gives blue or bluish-black microbes in a background tinged faintly yellow.

Indol Reaction.—Indol, C_8H_7N , more properly indine, is a weak base, which is a product of the growth of many species of microbes, and the detection of it may, therefore, be utilized as a differentiation test. S. Kitasato (*Zeit. f. Hyg.* VII, 518) gives the following method for performing the test:—

Ten c. c. of an alkaline-peptone-meat infusion (without gelatin), which has been previously inoculated with the microbes to be tested, and kept for twenty-four hours at blood heat, are treated with 1 c. c. of solution of pure potassium nitrate (0.02 gm. in 100 c. c.) and then with a few drops of concentrated sulphuric acid. In the presence of indol a rose or deep-red color is developed. *Spirillum cholerae* gives the reaction strongly; *S. Finkleri* feebly; *Bacillus typhosus* does not give it.

Inferences from Culture.—Several difficulties interfere with the interpretation of bacteriological cultures.

All natural waters contain microbes, the proportion being subject to great variation, without corresponding variation in sanitary quality. Many of the forms are harmless in any proportion. Their number is subject to rapid increase for a brief period after collection of the sample, and may be greatly modified by incidental conditions during storage or transportation, so that little value can be attached to quantitative determinations, except when made without appreciable delay. The culture fluids used, and the conditions under which the cultivation takes place, do not suffice for the development of all the forms present. The cultivation ought to be extended over many days and different samples of the same water tried with various nutritive media and at various temperatures, to secure a full knowledge of the microbes present.

As an indication of the insufficiency of these methods, it may be mentioned that Miller has described six species of microbes occurring in the human mouth, not one of which will grow in any form of culture medium at present known.

While, then, these examinations are as yet of uncertain value in the determination of the potability of water, they have been of much value in determining the effects and usefulness of certain conditions to which water is subjected. In these studies the method is sufficiently free from fallacy to make the results trustworthy. By it, it has been shown that filtration at first greatly diminishes the number of microorganisms, but subsequently, owing to the fouling of the filter, and partly to the penetration of successive colonies of microbes through the pores of the filter, the filtrate becomes richer in microbes than the unfiltered water. When suspended mineral matters are caused to

settle, a large proportion of the microbes is carried down ; but if the water thus purified is not soon removed, the microbic life again develops, it may be even in greater amount than was originally present. The storage of water at first increases and then diminishes the number present. The presence of free acid, even of carbonic acid, is decidedly inhibitory to their development. When microbes essentially foreign to the water are introduced they are often soon destroyed, apparently under the influence of those forms naturally present, and therefore, better adapted to existing conditions ; but this is by no means always the case, some of the more virulent pathogenic organisms having high resisting power.

Max Holz (*Zeit. f. Hyg.*, VIII, 159) gives a method of preparing a potato-gelatin, in which he finds the typhoid bacillus to grow freely. If such a culture medium be treated with 0.05 per cent. of pure phenol, it is found that the growth of moulds and liquefying bacilli is prevented while the growth of the *B. typhosus* is merely somewhat delayed.

CULTURE PHENOMENA OF SOME OF THE MORE IMPORTANT MICROBES.

Compiled from Macé and others.

| | ACTION ON GELATIN. | ON POTATO. | RELATION TO OXYGEN | REMARKS |
|--|---------------------------|--|-----------------------|---|
| <i>Bacillus butyricus</i> , . | Liquefies. | . . | Anaërobe. | Produces butyric acid. |
| <i>Bacillus chlorinus</i> , . | Liquefies. | . . | Aërobe. | Produces a green color. |
| <i>Bacillus cœruleus</i> , . . | Liquefies. | Dark bluish film. | Aërobe. | Produces blue color. |
| <i>Bacillus coli-commune</i> , | Does not liquefy. | Yellowish-green film. | Aërobe. | Not colored by Gram's method. |
| <i>Bacillus erythrosporus</i> , | Does not liquefy. | Reddish film. | Aërobe. | . . . |
| <i>Bacillus flavus</i> , . . . | Liquefies. | . . | Aërobe. | Forms a yellowish deposit. |
| <i>Bacillus fluorescens liquefaciens</i> , . . . | Liquefies. | Glistening yellow film. | Aërobe. | Strong green fluorescence. |
| <i>Bacillus fluorescens putidus</i> , | Does not liquefy. | . . | Aërobe. | Greenish fluorescence. |
| <i>Bacillus subtilis</i> , . . | Liquefies slowly. | Cream-col'd film. | Aërobe. | Occurs in hay infusion. |
| <i>Bacillus typhosus</i> , . . | Does not liquefy. | Thin, glairy film, harsh and resisting. | Facultative anaërobe. | Not colored by Gram's method; does not give indol reaction. |
| <i>Bacillus violaceus</i> , . . | Liquefies rapidly. | Brownish film. | Aërobe. | Violet color produced only in the presence of oxygen; reduces nitrates to nitrites. |
| <i>Micrococcus aquatilis</i> , | Does not liquefy. | . . | Aërobe. | Colonies white and crenate. |
| <i>Micrococcus prodigiosus</i> , | Liquefies. | Blood red. Old cultures have greenish lustre. | Aërobe. | Generally introduced from the air. |
| <i>Spirillum cholerae</i> , . | Slowly liquefies. | Grows only at moderately high temperature, as a thin brownish film. | Obligatory aërobe. | Not colored by Gram's method. Gives indol reaction. |
| <i>Spirillum Finkleri</i> , . | Liquefies rather rapidly. | Grows at ordinary temperature as a gray film with white ragged margin. | Aërobe. | Gives indol reaction feebly. |

PURIFICATION OF DRINKING WATER.

The most obvious method of purifying water is by distillation. The process is too expensive for general use, but is especially adapted for water intended for pharmaceutical or chemical purposes. It has also been used for supplying vessels at sea and in tropical localities in which the natural waters may be contaminated with malarial or other germs. The majority of microbes are killed by short exposure to a temperature of 212° F. ; hence, water may be purified, on a small scale, by simple boiling. Freezing does not have the same effect, many microbes retaining vitality for a long while in ice.

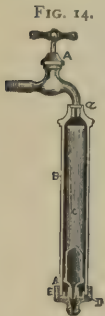
The self-purification of water, that is the destruction of organic matter and pathogenic microbes, by reason of the development of the ordinary microbes of putrefaction, occurs satisfactorily only in alkaline waters, hence, acid effluents check this process. The addition of lime in sufficient amount to give a slightly alkaline reaction will be beneficial.

The methods in general use for purifying water are simple filtration and the removal of the impurities by appropriate chemical agents.

Filtration.—For household purposes forms of carbon, stone and sand filters are used, which yield clear filtrates, but permit, sooner or later, the transmission of microbes. The suspended matter in the water gradually accumulates on the surface of the filter, and causes a great increase in the number of the microbes, some species of which apparently grow through the pores of the filter, and are carried into the filtrate. The following are among the more efficient forms of household filters:—

Bischof Spongy-Iron Filter.—The construction of this is shown in Fig. 13. The spongy iron is obtained by reducing hæmatite, at a temperature below the fusing point of iron.

It rests on a layer of pyrolusite (manganese dioxide), below which is an asbestos bag having a short tube with perforated cap. This is a very efficient form, removing much of the dissolved organic matter, and practically all the suspended matter, including the microbes.



Chamberlain-Pasteur Filter.—This consists of

tubes of unglazed biscuit-ware, the number depending on the size and required delivery of the filter. Fig. 14 shows the arrangement for continuous filtration by attaching the tube to the faucet. Fig. 15 shows a

form adapted to simultaneous cooling and filtration. The observations of Pasteur and others have shown that this is a highly efficient filter, yielding for a considerable time a filtrate entirely sterile. It requires occasional cleaning, since, after continuous use, the microbes may pass through the pores, probably by a process of growth. An occasional boiling of the tubes in water would be sufficient to overcome this difficulty.

FIG. 13.

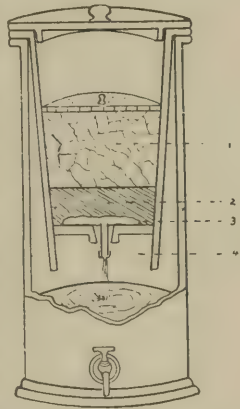
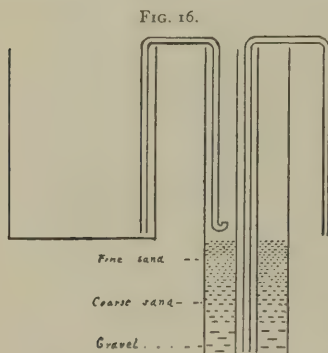


FIG. 15.



Fig. 16 shows a form of sand filter which is used in the laboratory of Professor Kemna, at Antwerp. A moder-



ately wide and stout tube is passed to the bottom of a tall jar, and the intervening space filled to the depth of about twenty-five centimeters with fine sand, coarse sand and gravel, as shown. The exit tube consists of a siphon, the outer leg of which does not quite reach to the level of the surface of the sand, the inner leg reaching to the bottom of the jar. The flow

may be controlled by a stop-cock attached to the outer leg. The object of this arrangement is to prevent the water level being drawn to or below the level of the sand. The filter should be supplied from a reservoir by means of a siphon, the exit tube of which is curved upward, in order to prevent disturbing the deposit which collects on the surface of the filter.

The filter may be cleaned by removing the siphon and sending a slow current of water down the wide tube until the deposit upon the surface of the sand is washed out. The apparatus is especially suited for laboratory experiments on filtration.

For the purification of drinking water on a large scale, sand filter beds have been found to be efficient; but the best results are obtained only under proper supervision.

Numerous determinations of the efficiency of sand filtering basins have been made by bacteriological and chemical

methods. It has been found that, at the start, a large proportion of the organic matter, dead and living, passes through; but that as filtration proceeds, the surface of the sand becomes covered with a close deposit, which acts both as a means of retaining suspended impurities and, by its active microbic life, destroys the organic matter in a manner analogous to that occurring in soil. The water thus becomes practically free from microbes, but after a time these gradually penetrate the pores of the filter and appear in the filtrate. Increase of pressure will hasten this effect.

Bertschinger (*Jour. Soc. Chem. Ind.*, Dec. 1889; abstract) has published observations on the efficiency of the sand filters in use at the Zürich Public Water-works. The filtering material rests on a brick grating, and consists of the following layers, commencing at the bottom:—

5 to 15 cm. of coarse gravel, 10 cm. of garden gravel, 15 cm. of coarse sand and 80 centimeters of fine sand. As soon as the diminution in pressure of water, due to the resistance of the filter, is from 60 to 80 cm., the filter is cleaned by allowing the water to run off and removing the top layer of sand to a depth of 2 cm., as this is found to contain the whole of the mud. The filter is then filled up with filtered water from below, and washed by allowing this to overflow. After filtration has recommenced, the first portion of the filtrate is rejected. Two of the filters are arched over; these require cleaning once in seventy-seven days; the others once in forty-eight days. As soon as the layer of fine sand has been reduced to the thickness of 50 cm., fresh sand is substituted or more added, until the depth is again 80 cm. Among the conclusions reached are the following:—

Under normal conditions the filtered water is free from

microbes, although a few are taken up again in the later stages of the filtration.

After cleaning the filter, the water which first passes through is not in normal condition. It contains many microbes, the efficient layer of scum not having had time to collect on the sand, though the chemical purity of the water is satisfactory.

When the filters have not been used for some time, the water which first passes through them contains more bacteria than usual, owing to their rapid multiplication in stagnant water, but its chemical purity is not materially different from the normal filtered water.

Precipitation Methods.—The observations of Dr. P. F. Frankland and others, have established the following points:—

“Organized matter is, to a large and sometimes to a most remarkable extent, removable from water by agitation with suitable solids in a fine state of division, but such methods of purification are unreliable.

“Chemical precipitation is attended with a large reduction in the number of microorganisms present in the waters in which the precipitate is made to form and allowed to subside.

“If subsidence either after agitation or after precipitation be continued too long, the organisms first carried down may again become redistributed throughout the water.”

It is essential, therefore, that the liquid be filtered as short a time after the precipitation as possible.

A small quantity of alum added to water is decomposed with the formation of a flocculent precipitate of aluminum hydroxide, which settles comparatively rapidly, and carries down with it all suspended matters, as well as a large

proportion of the dissolved organic matters. Waters which contain such an excess of organic matter as to be distinctly colored, may usually be made quite clear and colorless by this treatment. Two grains of alum to the gallon will suffice for the purpose, but if very rapid subsidence is desired more may be added.

Several systems of filtration now in extended use employ this precipitation method in conjunction with filters of small area, the necessary flow being obtained by increased pressure. The Hyatt and National systems belong to this class. The differences between the various forms are chiefly in the mechanical arrangements for supplying the water and for cleaning the filter. The material is generally sand or coke; the cleaning is performed at short intervals, by means of reverse currents of water. The alum solution is introduced as needed by automatic apparatus.

These filters are efficient, and are suitable for the purification of water for manufacturing establishments, and when large basins are not available.

The addition of an iron salt to water containing carbonates, is attended with decomposition and the formation of a precipitate of ferric hydroxide. This reaction has been employed with great advantage as a means of purification. One of these methods was by passing the water through spongy iron, then aerating to precipitate the iron, and filtering through sand. The method is very efficient, but the spongy iron gradually chokes by oxidation, and becomes useless. This difficulty is removed by the use of iron borings or punchings, contained in an iron cylinder (Anderson and Ogston, *Proc. Inst. Civ. Eng. Vol. 81*), which is rotated while the water passes through; the iron is brought into

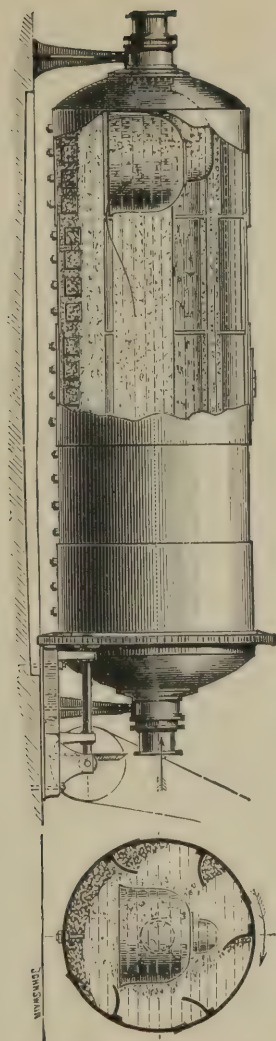
thorough contact with the water, and there is sufficient abrasion to keep its surface clean.

The apparatus as practically employed is shown in Fig. 17. It consists of a cylinder rotating in a horizontal position, attached to the internal periphery of which are short curved shelves, arranged at equal distances. Pipes enter the hollow trunnions to admit and discharge the water. As it enters the cylinder, the water strikes against a circular distributing plate, and is caused to flow radially through a narrow annular space, to prevent the formation of a central current along the axis of the purifier. The inner end of the outlet pipe carries an inverted bell-mouth which catches the fine particles of the iron carried forward by the water, and causes them to fall again to the bottom of the cylinder. Sufficient borings or punchings to one-tenth fill the cylinder are introduced, and the purifier is then completely filled with water, and set in motion, the rate of rotation being about six feet per minute at the periphery. The effect of the rotation is to scoop up the iron particles and to shower them down through the flowing water.

The effect is due mainly to the formation of ferrous carbonate, through the action of the carbonic acid of the water. On issuing into the open air, this is gradually converted by oxidation into the insoluble ferric hydroxide, which carries down much of the organic matter and subsequently oxidizes and destroys it. Temporary hardness is also decreased by the abstraction of the carbonic acid and consequent precipitation of calcium and magnesium carbonates.

The time of contact with the iron depends upon the purity of the water. For Antwerp water, which is purified by this means, the maximum effect is accomplished in 3.5

Fig. 17.



minutes. After leaving the cylinder, the water is passed through sand filters. Analytical examinations show the effluent water to be of high organic purity and practically sterile.

Cast-iron borings are much more readily acted upon than steel punchings. The latter suffice in operating upon water rich in dissolved organic substances, carbon dioxide and suspended matters, while the former are especially suited for treatment of water comparatively pure, and, therefore, less active.

For determining the most advantageous method of treating any water supply, laboratory experiments may be made as follows:—

A strong wide-mouth bottle holding about 2000 c. c., is charged with one-tenth its bulk of clean borings or punchings, filled completely with water and shaken for four minutes, in such manner that the iron particles are continuously showered through the liquid. The water is then aërated by agitating it in a large, thoroughly clean glass-stoppered bottle. With some (*e. g.*, peaty) waters, it will be of advantage to allow about 200 c. c. of air to remain in the bottle in which the shaking with iron is performed, occasionally removing the stopper to renew the air. (Continuous aëration during treatment is provided for in the apparatus used on the large scale). The liquid is allowed to stand from a few minutes to four hours, depending on the rapidity with which the iron separates, and is then filtered through the sand filter (page 100), or through a well-washed cotton plug inserted in the neck of a funnel. Satisfactory purification as regards ammonium compounds cannot be obtained, but with proper attention to cleanliness, the figures for total organic nitrogen, nitrogen by permanganate, and oxygen consuming power will be trustworthy.

The following results were obtained by us in the treatment of Delaware river water at Lardner's Point pumping station, Philadelphia. The purifier was capable of delivering 100,000 gallons per 24 hours. All figures are in parts per million.

September, 1890.

| | Before Treatment. | After Treatment. |
|-----------------------|-------------------|------------------|
| Nitrogen as ammonium, | .04 | .03 |
| “ as permanganate, | .27 | .09 |

November, 1890.

| | | |
|-----------------------|---------|-------|
| Nitrogen as ammonium, | .084 | .034 |
| “ by permanganate, | .091 | .049 |
| “ as nitrites, | traces. | none. |

A sample of Schuylkill water treated in the laboratory, and the reduction of total organic nitrogen determined, gave the following figures:—

| | Before Treatment. | After Treatment. |
|-------------------------|-------------------|------------------|
| Total organic nitrogen, | 0.36 | 0.118. |

Sample of water from the Mississippi river at Memphis Tenn.

| | Before Treatment. | After Treatment. |
|----------------------------|-------------------|------------------|
| Oxygen absorbed at 212°F., | 2.88 | 0.36 |

IDENTIFICATION OF THE SOURCE OF WATER.

The determination of the course of underground streams, and of communications between collections of water, is often an important practical problem. In geological and sanitary surveys, valuable information may occasionally be gained. The method generally pursued when connection between water at accessible points is to be detected, is to introduce at one point some substance not naturally existing in the water, and capable of recognition in small

amount. Lithium compounds are among the best for this purpose. They are not frequent ingredients of natural waters, and are easily recognized by the spectroscope. Lithium chloride is the most suitable. The quantity to be employed will vary with circumstances. It scarcely needs to be stated that the waters under examination should be carefully tested for lithium before using the method.

When the lithium method is inadmissible, recourse must be had to other substances of distinct character, such as strontium chloride, but this possesses the disadvantage that a considerable amount may be rendered insoluble, and thus lost in the ordinary transit through soil. Recently, use has been made of organic coloring matters of high tinctorial power, one of the most suitable of which is *fluoresceïn*, $C_{20}H_{12}O_5$, a derivative of benzene. This will communicate a characteristic and intense fluorescence to many thousand times its weight of water. An entire river may be colored by a few kilograms. By its use an underground communication was demonstrated to exist between the Danube and the Ach, a small river which flows into the Lake of Constance. The coloration is only distinct in alkaline liquids. Other colors, such as aniline red, may be employed. For detecting leakage from cesspools and cisterns, sanitary inspectors occasionally employ water colored by Prussian blue.

A more important feature of the problem in a sanitary point of view is the determination of the source of a given current or collection of water, when such source is inaccessible. Problems of this character are not infrequent in large cities in which the systems of water supply and drainage are defective, thus giving occasion to accumulations of water in cellars and similar places. Often, in these cases, no ex-

tended explorations can be made, by reason of the adjacent buildings and conflicting property interests, and the question may arise whether the water proceeds from a leaky hydrant, drain, sewer, or subsoil current. It is obvious that in the case of the collection of water in a cellar from causes other than surface washings or entrance of rain, it must have passed through some distance of soil, and in built-up districts will almost certainly be charged with organic refuse. To correctly interpret the results, it will be necessary to know the general character of the subsoil water of the district and the composition of the public supply. As a rule, the transmission of water through moderate distances of soil will not materially increase the mineral constituents. Hence, if the sample contains an excess of dissolved matters as compared with the water supply of the district, it may reasonably be inferred that it is derived from a drain, sewer, or subsoil current.

In these investigations it will generally be sufficient to determine the total solids, odor on heating, chlorine, nitrates and nitrites. The following figures are from some results obtained in investigations made in association with Mr. Chas. F. Kennedy, Chief Inspector to the Board of Health of this city :—

| | CITY SUPPLY. | CELLAR WATER. | | |
|--------------------------|--------------|---------------|---------|---------|
| | | No. 1. | No. 2. | No. 3. |
| Total solids, | 115 | 140 | 661 | 640 |
| Odor on heating, . . . | faint | faint | strong | urinous |
| Chlorine, | 4 | 6.4 | 77.0 | 128.0 |
| N as nitrates, | 0.7 | 1.0 | 3.5 | none |
| “ “ nitrites, | none | present | present | none |

Sample No. 1 was taken from a cellar in which a small amount of water had been almost constantly present for a

long time, and of which the source could not be ascertained. The results of analysis led to the view that since it resembled in composition the city supply, it was derived from a leaky hydrant pipe. The parties in interest were not inclined to accept this opinion, but the examination of the condition of the hydrant on an adjacent property showed a leak, which being repaired the water ceased to appear in the cellar. In this case it was found that the water had passed through twenty-two feet of earth. In the second case the sample is seen to be very impure, and it was suggested that it was derived directly from a leaky drain, which upon exploration proved to be the case. In the third sample, the high chlorine, strong urinous odor and absence of nitrates and nitrites pointed unmistakably to recent and profuse contamination with sewer water.

Occasionally the analytical results will be ambiguous, and it is advisable to make examinations of more than one sample, since accidental circumstances, rain-fall, etc., may affect the composition of the water.

Instances of the contamination of water by unusual substances are occasionally noted, and these sometimes afford a clue to the source of the water. Among the instances of this kind within our own experience may be noted the contamination with petroleum and with soap. In the former case it was evident that the contamination was from a leaky pipe connecting two refineries. In the latter it was shown to be derived from an adjoining building used as a laundry.

TECHNICAL APPLICATIONS.

Boiler Waters.—The main conditions affecting the value of a water for steam making purposes are its tendency to cause corrosion and the formation of scale. *Corrosion* may be due to the water itself, to the presence of free acids, or to substances which form acids under the influence of the heat to which the water is subjected. Pure water, *e. g.*, distilled water, exhibits a powerfully corrosive action upon iron. The dissolved oxygen which all waters contain also aids in the corrosion, and especially when accompanied, as is usually the case, by carbonic acid. There is always greater rusting at the point at which the water enters the boiler, since there the gases are driven out of solution and immediately attack the metal. This is an evil that obtains with all waters, and it is not customary, in making examination for technical purposes, to determine the amount of these bodies. In water that has had free access to air, the oxygen in solution is a tolerably constant quantity, and it is sufficient to note the temperature and refer to the table of amounts of oxygen dissolved in water. The corrosive action of oxygen and carbonic acid is especially noticeable in waters that are comparatively pure, such as those derived from mountain springs. This was repeatedly observed by one of us in the examination of the waters used for the locomotives of the Baltimore and Ohio railroad. The waters which caused the most corrosion were mainly those containing small quantities of solid matter, the full amount of oxygen and considerable carbonic acid, but no other acid or acid-forming body.

Free acid, other than carbonic acid, is not often found in water, and if present renders the water unfit for use,

unless it be neutralized. Mine waters are the most likely to contain free acid, sulphuric acid being generally present. Sometimes the acidity is due to organic acids. These act very injuriously on iron. Allen gives an example of this in the water supplied to Sheffield, Eng., which he found to contain an organic acid in amount equivalent to from 3.5 to 10 parts of sulphuric acid per million.

Magnesium chloride is frequently present in waters, and if in considerable quantity may be very harmful. At a temperature of 310° F., corresponding to an effective pressure of four atmospheres, magnesium chloride reacts with water to form magnesium oxide and hydrochloric acid, the latter attacking the boiler, especially at the water line. If there is present at the same time considerable calcium carbonate the evil may be somewhat lessened, but as Allen has pointed out, and as we also have noticed, there may still be corrosion, so that the presence of more than a small quantity of the salt, say a grain or two to the gallon, may be considered objectionable. Allen remarks that the presence of a certain amount of sodium chloride may prevent this decomposition, the two chlorides combining to form a stable double salt. The addition, therefore, of common salt to a water containing magnesium chloride may act to diminish corrosion, a point which will bear further investigation.

It has not been determined how far the presence of nitrites, nitrates and ammonia affects the quality of water for steam-making purposes; but it is more than probable that they act harmfully, especially the nitrates, which are frequently present in large amount.

Scale is composed of matters deposited from the water either by the decompositions induced by the heat or by

concentration. When the deposit is loose it is termed *sludge* or *mud*, and usually consists of calcium carbonate, magnesium oxide and a small amount of magnesium carbonate. The magnesium oxide is formed by the decomposition of the magnesium carbonate and chloride. This fact was first pointed out by Driffield (*J. Soc. Chem. Ind.*, VI, 178).

The formation of sludge is the least objectionable effect, since it may readily be removed by "blowing off," provided that care is previously taken to allow the flues to cool down so that when the water is removed the heat of the flues may not bake the deposit to a hard mass. Waters containing calcium sulphate form hard incrustations difficult to remove and causing great loss of fuel by interfering with the transmission of the heat to the water. It not only forms a hard incrustation in itself, but becomes incorporated with the mud and renders it also hard. The hard scale will also contain practically all the silica and the iron and aluminum present in the water, besides any matters originally held in suspension.

It follows from the above that a water only temporarily hard, will, if care is taken in the management of the boiler, cause the formation merely of a loose deposit of sludge—temporary hardness being due in the main to calcium and magnesium carbonates. A water permanently hard will probably form a hard scale, since such hardness is usually due to calcium sulphate.

In accordance with these principles, the analysis of a water for steam-making purposes may include the determinations of free acid, total solid residue, SO_4 , Cl , Ca , Mg , temporary and permanent hardness. In cases in which the qualitative tests show but small amounts of SO_4 and Cl ,

the analysis may be limited to the determinations of the temporary and permanent hardness.

It has been pointed out in an earlier chapter that it is not possible to deduce from the analytical result the exact forms in which the various elements are combined, but since it is known that at the high temperature ordinarily reached in boilers definite chemical changes occur, it is safest to exhibit the maximum amount of corrosive and scale-forming ingredients which the water under these circumstances could develop. Thus, since calcium sulphate is practically insoluble in water above 212° F., the proportion of calcium sulphate may be regarded as such as would be formed by the total quantity of calcium or the total quantity of SO_4 , according to which is present in the larger amount. Similarly, as the decomposition of magnesium chloride is induced by the high temperature of the boiler, the analytical statement should indicate the maximum proportion of this compound obtainable from the magnesium and chlorine present. These rules cannot apply absolutely to waters rich in alkali carbonates, since these would neutralize any acid formed from the magnesium chloride, or even prevent its formation, and would prevent to a large extent the formation of calcium sulphate. Much remains to be determined concerning the effects of the high temperature and concentration to which boiler waters are subjected.

Purification of Boiler Waters.—The problems present in the treatment of boiler waters are usually the removal of the calcium carbonate and sulphate, and magnesium carbonate and chloride. Both carbonates are appreciably soluble in pure water. About one grain of calcium carbonate to the gallon is usually stated to be the

proportion dissolved, but it has been pointed out by Allen that solutions can be obtained containing twice this amount. If the water contains carbonic acid it will take up a much greater proportion of the carbonates, but in this case they will be deposited from the solution by boiling. This has been accounted for by supposing the existence of soluble bicarbonates, which are decomposed by the boiling. Nearly all of these carbonates can be thrown out of solution by any means that will deprive the water of the carbonic acid. Sodium hydroxide is usually the best for the purpose, and should be added in quantity just sufficient to form normal sodium carbonate. If there are present in the water calcium and magnesium chlorides and sulphates, these also will be decomposed and precipitated by the sodium carbonate so formed. If the amount of sodium carbonate formed is not sufficient to decompose all of these bodies, a sufficient quantity should be added with the sodium hydroxide to effect the complete decomposition. The precipitate is allowed to settle or filtered off.

In cases in which the feed-water is heated before it enters the boiler, it may only be necessary to add to the water sodium carbonate in quantity sufficient to decompose the calcium and magnesium chlorides and sulphates, since the heat alone will suffice to throw down the carbonates.

Care should be taken in these precipitations that no more sodium hydroxide is added than is required for the precipitation, since any excess would tend to corrode the boiler.

Clark's process consists in treating the water with calcium hydroxide (lime-water). This precipitates the calcium and magnesium carbonates by depriving the water of its free carbonic acid. It has, of course, no effect upon the cal-

cium sulphate. It is to be noted that the proportion of calcium hydroxide which is to be added must be calculated from the amount of free carbonic acid existing in the water, and not from the amount of carbonates to be removed. The precipitate will usually require at least twelve hours for complete subsidence, but after three or four hours the water will be sufficiently clear for some purposes. If a filter press is used, as in Porter's process, the time required for clarification is very much shortened. Another advantage of this process is the use of a solution of silver nitrate, in order to determine more conveniently the proportion of calcium hydroxide which is to be employed. The lime is first slaked and dissolved in water, and the water to be softened run in and thoroughly mixed with it. From time to time small portions are taken out and a few drops of a solution of silver nitrate added. As long as the lime is in excess a brownish coloration is produced. When this has become quite faint, and just about to disappear, the addition of the water is discontinued, and, after a short time, the water is filtered by means of the press.

Soluble phosphates added to a water, precipitate completely in a flocculent condition any calcium, magnesium, iron or aluminum. This reaction can be best applied by using the tri-sodium phosphate ($\text{Na}_3\text{PO}_4 + 12\text{H}_2\text{O}$), which is now a commercial article. By reason of the facility with which this substance loses a portion of its sodium to acids, it acts not only as a precipitant to the above materials, but will neutralize any free mineral acid present in the water. From evidence submitted by those who have used the process on the large scale, it appears that not only is no hard scale formed, but that scale already existing prior

to its use is gradually disintegrated and removed with the sludge. Experiments indicate that no injury results from an excess of the material ; but the economical employment of the method, especially with very hard waters, can only be based upon a correct analysis, and an estimation of the phosphate required for the precipitation. In many cases the composition of the water will be such that a partial precipitation will be sufficient.

Waters rich in ferrous compounds may be purified by thorough aëration and filtration, the iron being separated as ferric hydroxide. Simple filtration through a bed of manganese dioxide will accomplish the same purpose.

General Technical Uses.—In regard to the quality of water for technical other than steam-making purposes, such as brewing, dyeing, tanning, etc., no detailed methods or standards can be laid down. The nearest approach to purity that can be secured in the supply will be of the greatest advantage. The more objectionable qualities will be large proportion of organic matter, especially if it distinctly colors the water, excessive hardness, and notable amounts of iron or free mineral acid. It is stated by Bell (*Jour. Soc. Chem., Ind.*) that one part per million of iron will render water unsuitable for bleaching establishments. It has been noted that a large proportion of active microbes is injurious in the manufacture of indigo. In artificial ice making, a very pure water must be used if a clear and colorless product be desired. Any suspended or dissolved coloring matter will be concentrated by the freezing and appear in the bottom or centre of the mass. The Antwerp water, purified by the Anderson process, is

used with entire satisfaction for the manufacture of artificial ice in that city.

The examination of sewage effluents and waste waters from manufacturing establishments is to be conducted upon the same principles as for ordinary supplies, but especial attention must be given to the presence of poisonous metals, and free mineral acids. The latter interfere with the normal self-purification of the water. For the nitrogen determination, the Kjeldahl process will be found more satisfactory than that by alkaline permanganate.

•

ANALYTICAL DATA.

FACTORS FOR CALCULATION.

| | | | | |
|-----------|-------------|-----------------|---|--------------------------------|
| Parts per | 100,000 | $\times .7$ | = | Grains per Imperial Gallon |
| " " | 1,000,000 | $\times .07$ | = | " " " " |
| " " | 100,000 | $\times .583$ | = | " " U. S. " |
| " " | 1,000,000 | $\times .058$ | = | " " " " |
| " " | 1,000,000 | $\times .00833$ | = | Av. pounds per 1000 U. S. Gal. |
| Grains " | Imp. gallon | $\div .7$ | = | Parts per 100,000 |
| " " | " " | $\div .07$ | = | " " 1,000,000 |
| " " | U. S. " | $\div .583$ | = | " " 100,000 |
| " " | " " | $\div .058$ | = | " " 1,000,000 |

| | | | |
|---|----------------|---|---------------|
| Al_2O_3 , | $\times .534$ | = | Al |
| AgCl , | $\times .2473$ | = | Cl |
| BaSO_4 , | $\times .588$ | = | Ba |
| BaSO_4 , | $\times .1373$ | = | S |
| BaSO_4 , | $\times .412$ | = | SO_4 |
| B_2O_3 , | $\times .3143$ | = | B |
| CaO , | $\times .7143$ | = | Ca |
| CaCO_3 , | $\times .40$ | = | Ca |
| Fe_2O_3 , | $\times .7$ | = | Fe |
| KCl , | $\times .524$ | = | K |
| $\text{Mg}_2\text{P}_2\text{O}_7$, | $\times .2162$ | = | Mg |
| $\text{Mg}_2\text{P}_2\text{O}_7$, | $\times .856$ | = | PO_4 |
| MnS , | $\times .632$ | = | Mn |
| NaCl , | $\times .394$ | = | Na. |

CONVERSION TABLE.

| PARTS PER MILLION. | GRAINS PER U. S. GALLON. | GRAINS PER IMP. GAL. | PARTS PER MILLION. | GRAINS PER U. S. GALLON. | GRAINS PER IMP. GAL. |
|--------------------------|-----------------------------|----------------------------|--------------------------|-----------------------------|----------------------------|
| 1 | .058 | .07 | 26 | 1.508 | 1.82 |
| 2 | .116 | .14 | 27 | 1.566 | 1.89 |
| 3 | .174 | .21 | 28 | 1.624 | 1.96 |
| 4 | .232 | .28 | 29 | 1.682 | 2.03 |
| 5 | .290 | .35 | 30 | 1.740 | 2.10 |
| 6 | .348 | .42 | 31 | 1.798 | 2.17 |
| 7 | .406 | .49 | 32 | 1.856 | 2.24 |
| 8 | .464 | .56 | 33 | 1.914 | 2.31 |
| 9 | .522 | .63 | 34 | 1.972 | 2.38 |
| 10 | .580 | .70 | 35 | 2.030 | 2.45 |
| 11 | .638 | .77 | 36 | 2.088 | 2.52 |
| 12 | .696 | .84 | 37 | 2.146 | 2.59 |
| 13 | .754 | .91 | 38 | 2.204 | 2.66 |
| 14 | .812 | .98 | 39 | 2.262 | 2.73 |
| 15 | .870 | 1.04 | 40 | 2.320 | 2.80 |
| 16 | .928 | 1.12 | 41 | 2.378 | 2.87 |
| 17 | .986 | 1.19 | 42 | 2.436 | 2.94 |
| 18 | 1.044 | 1.26 | 43 | 2.494 | 3.01 |
| 19 | 1.102 | 1.33 | 44 | 2.552 | 3.08 |
| 20 | 1.160 | 1.40 | 45 | 2.610 | 3.15 |
| 21 | 1.218 | 1.47 | 46 | 2.668 | 3.22 |
| 22 | 1.276 | 1.54 | 47 | 2.726 | 3.29 |
| 23 | 1.334 | 1.61 | 48 | 2.784 | 3.36 |
| 24 | 1.392 | 1.68 | 49 | 2.842 | 3.43 |
| 25 | 1.450 | 1.75 | 50 | 2.900 | 3.50 |

DIRDIN'S TABLE OF OXYGEN DISSOLVED BY WATER AT VARIOUS TEMPERATURES, EXTENDED TO GIVE THE WEIGHT OF OXYGEN PER LITER. CORRECTED TO 0° C. AND 760mm. PRESSURE.

| TEMPERATURE FAHRENHEIT. | TEMPERATURE CENTIGRADE. | CUBIC INCHES OF OXYGEN PER GALLON (70000 GRAINS). | MILLIGRAMS OF OXYGEN PER LITER. |
|----------------------------|----------------------------|---|---------------------------------------|
| 41° | 5.00° | 2.101 | 10.84 |
| 42 | 5.55 | 2.074 | 10.72 |
| 43 | 6.11 | 2.048 | 10.57 |
| 44 | 6.66 | 2.022 | 10.45 |
| 45 | 7.22 | 1.997 | 10.30 |
| 46 | 7.77 | 1.973 | 10.18 |
| 47 | 8.33 | 1.949 | 10.06 |
| 48 | 8.89 | 1.927 | 9.94 |
| 49 | 9.44 | 1.905 | 9.83 |
| 50 | 10.00 | 1.884 | 9.72 |
| 51 | 10.55 | 1.864 | 9.61 |
| 52 | 11.11 | 1.844 | 9.51 |
| 53 | 11.66 | 1.826 | 9.42 |
| 54 | 12.22 | 1.808 | 9.33 |
| 55 | 12.77 | 1.791 | 9.24 |
| 56 | 13.33 | 1.775 | 9.15 |
| 57 | 13.89 | 1.760 | 9.08 |
| 58 | 14.44 | 1.746 | 9.01 |
| 59 | 15.00 | 1.732 | 8.94 |
| 60 | 15.55 | 1.719 | 8.87 |
| 61 | 16.11 | 1.706 | 8.80 |
| 62 | 16.66 | 1.695 | 8.74 |
| 63 | 17.22 | 1.683 | 8.68 |
| 64 | 17.77 | 1.674 | 8.64 |
| 65 | 18.33 | 1.667 | 8.60 |
| 66 | 18.89 | 1.660 | 8.56 |
| 67 | 19.44 | 1.652 | 8.52 |
| 68 | 20.00 | 1.644 | 8.48 |
| 69 | 20.55 | 1.639 | 8.45 |
| 70 | 21.11 | 1.634 | 8.43 |

The table is calculated for a barometric pressure of 760 mm., and would require corrections for variations from this, but such corrections are mostly within the limits of experimental error.

ANALYSES OF RAIN AND SUBSOIL WATERS.

PARTS PER MILLION.

| | From. | Total Solids. | Chlorine. | N by KMnO_4 . | N as NH_4 . | N as NO_2 . | N as NO_3 . |
|----------------|---|---------------|-----------|------------------------|----------------------|----------------------|----------------------|
| Rain water. | Bellefonte—collected by Prof. Wm. Frear, after long rain. | 5 | none | 0.148 | 0.280 | none | none |
| Subsoil water. | Wynnewood—pool fed by underground spring. | 65 | 6.20 | 0.032 | 0.024 | none | 2.3 |
| “ “ | Wynnewood—well about 150 yards from above. | 60 | 4.00 | 0.024 | 0.016 | none | 3.5 |
| “ “ | Wynnewood—well polluted by farm-yard drainage; about 500 yards from pool. | ... | 16.00 | 0.208 | 0.028 | none | 14.2 |
| “ “ | Pump-well in densely populated district. Highly contaminated. | 1120 | 57.00 | 1.00 | 3.120 | 0.01 | 33.0 |
| “ “ | Newly dug well in populated district. Highly contaminated. | 620 | 120.00 | 0.08 | 2.00 | 0.03 | 16.0 |
| “ “ | Well at Barren Hill, 130 feet deep. | 470 | 120.00 | undet. | undet. | traces | 22.0 |

RESULTS FROM SCHUYLKILL RIVER—PARTS PER MILLION.

Samples taken from hydrant at 715 Walnut Street.

| 1888. | State of Weather. | Condition. | Total Solids. | Nitrogen by KMnO_4 . | Nitrogen as NH_4 . | Nitrogen as NO_2 . | Nitrogen as NO_3 . |
|-----------|-------------------|-----------------------|---------------|-------------------------------|-----------------------------|-----------------------------|-----------------------------|
| Sept. 17. | Continued rain. | Turbid. | 160 | .06 | .048 | None. | .13 |
| " 18. | Continued rain. | Muddy. | 160 | .09 | .020 | " | .34 |
| " 19. | Clear. | Turbid. | 140 | .108 | .004 | Trace. | .34 |
| " 20. | " | " | 130 | .124 | None. | Faint trace. | .25 |
| " 21. | " | " | 130 | .132 | " | None. | .25 |
| " 22. | " | Less turbid. | 180 | .180 | " | Faint trace. | .25 |
| " 24. | " | Very muddy. | 140 | .100 | " | None. | .13 |
| " 25. | " | Turbid. | 130 | .092 | " | Faint trace. | .13 |
| " 26. | " | Slightly turbid. | 120 | .068 | .01 | " | .18 |
| " 27. | " | Very slightly turbid. | 110 | .056 | None. | " | .18 |
| " 28. | " | Very slightly turbid. | 105 | .052 | " | " | .36 |
| " 29. | " | Nearly clear. | 125 | .052 | .008 | " | .70 |
| Oct. 1. | " | " | 140 | .052 | .012 | " | .70 |
| " 2. | " | " | 125 | .044 | None. | " | .40 |
| " 3. | " | " | 120 | .080 | .016 | " | .68 |
| " 4. | " | Clear. | 120 | .084 | .008 | " | .80 |
| " 5. | " | " | 120 | .092 | .012 | " | .70 |
| " 6. | Rain. | " | 120 | .060 | .012 | " | .80 |
| " 8. | " | Turbid. | 150 | .108 | .008 | " | .80 |
| " 9. | Clear. | Slightly turbid. | 130 | .088 | .008 | " | .70 |
| " 10. | " | Almost clear. | 125 | .056 | .010 | " | .70 |
| " 11. | " | Clear. | 115 | .044 | .010 | " | .70 |

ANALYSES OF ARTESIAN WATERS.

MILLIGRAMS PER LITER.

| | PHILADELPHIA. | | | | | BALTIMORE. | INDIANA. | |
|-------------------------------|-----------------------|--------------------------|----------------------|-------------------------|-------------------------|-----------------|----------------|------------|
| | 9th and Chestnut Sis. | 24th and Washington Ave. | 15th and Walnut Sis. | Broad and Columbia Ave. | Broad and Chestnut Sis. | Black's Island. | Locust Point.* | Ft. Wayne. |
| Condition, | Clear. | Clear. | Slightly turbid. | Clear. | Clear. | Clear. | Clear. | Clear. |
| Reaction, | Alkaline. | Alkaline. | Alkaline. | Alkaline. | Alkaline. | Alkaline. | Alkaline. | Alkaline. |
| SiO ₂ , | 36.00 | 34.50 | 35.00 | 24.00 | 29.00 | 19.50 | 4.00 | .. |
| SO ₄ , | 61.80 | 36.26 | 9.90 | 25.84 | 15.24 | 102.36 | 4.10 | .. |
| PO ₄ , | 0.24 | 0.31 | 0.31 | Trace. | Trace. | 0.38 | .. | .. |
| CO ₂ (combined), . | 64.91 | 110.17 | 54.80 | 78.84 | 108.64 | 50.64 | .. | .. |
| Cl., | 89.21 | 91.77 | 108.50 | 206.01 | 172.00 | 554.48 | 4.68 | 190.2 |
| H ₂ S, | .. | Trace. | .. | .. | .. | .. | .. | .. |
| Mn, | .. | .. | .. | 1.80 | 4.32 | .. | .. | .. |
| Fe, | 9.80 | 7.70 | 5.70 | 5.28 | .. | 1.05 | .. | .. |
| Ca, | 54.57 | 44.28 | 50.00 | 125.00 | 101.42 | 53.57 | 2.5 | .. |
| Mg, | 15.27 | 7.98 | 12.60 | 30.70 | 22.27 | 6.48 | 0.86 | .. |
| Na, | 54.13 | 84.13 | 32.46 | 72.34 | 55.83 | 378.63 | .. | .. |
| K, | 4.14 | 8.54 | 4.10 | Traces. | 0.28 | Trace. | .. | .. |
| N by KMnO ₄ , . . | 0.032 | Not det. | 0.048 | 0.048 | 0.015 | 0.148 | 0.012 | 0.035 |
| " as NH ₄ , . . | 0.248 | Not det. | 0.034 | 0.032 | 0.004 | 0.132 | 0.044 | 0.315 |
| " " NO ₂ , . . | Trace. | None. | None. | 0.02 | Trace. | None. | None. | None. |
| " " NO ₃ , . . | Trace. | Trace. | None. | 2.00 | 1.00 | None. | None. | None. |

* We are indebted to Mr. Wm. Glenn, Chemist of the Baltimore Chrome Works, for this sample.

TABLE SHOWING THE RELATIVE PURITY OF THE WATER SUPPLIED
TO CITIES, FROM THE DETERMINATIONS MADE IN
JUNE, 1881, BY A. R. LEEDS.

| Parts per million. | Philadelphia. | New York. | Brooklyn. | Jersey City. | Boston. | Washington. | Rochester. | Cincinnati. |
|--|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|
| Total solids, | 143.0 | 118.0 | 60.0 | 93.0 | 85.0 | 115.0 | 100.0 | 162.0 |
| " hardness, | 44.0 | 33.0 | 22.7 | 32.0 | 21.0 | 48.0 | 55.0 | 64.0 |
| Chlorine, | 3.0 | 3.5 | 5.5 | 2.35 | 3.15 | 2.70 | 1.95 | 8.05 |
| Oxygen-consuming power, | 4.6 | 8.1 | 4.13 | 9.5 | 17.7 | 6.00 | 7.9 | 8.6 |
| Nitrogen by KMnO_4 , Nitrogen in amm o- nium compounds. . | .147 .008 | .221 .022 | .067 .006 | .344 .039 | .496 .108 | .221 .049 | .188 .093 | .196 .094 |
| Nitrogen as nitrites. " " nitrates. | None. 1.51 | None. 1.84 | None. 2.69 | None. 2.01 | None. 2.75 | None. 1.84 | None. 1.39 | None. 1.64 |

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